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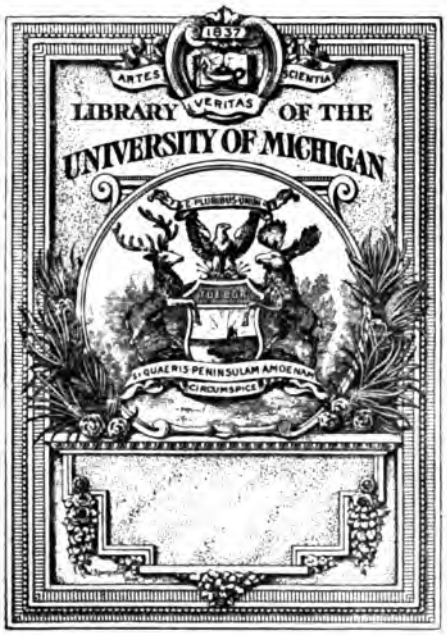
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UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 40: THE OXALATES OF BISMUTH,
BY E. G. ALLAN
(From Transactions of the Royal Society of Canada, Series III., Vol. II.)

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V.—*The Oxalates of Bismuth.*

By DR. F. B. ALLAN.

(Communicated by Prof. W. Lash Miller, and read May 19th, 1903.)

Neutral oxalate of bismuth Bi_2O_3 3 C_2O_3 7½ H_2O was prepared by Souchay and Lensson (Ann. der Chem., 105, 245), by adding oxalic acid to a solution of bismuth oxide in nitric acid. It was also prepared by Muir (Jour. of the Chem. Soc. 1878, 193), who gave it the formula Bi_2O_3 3 C_2O_3 6 H_2O. Swartzenburg (Ann. der Chem. 64, 127) boiled bismuth oxide with acid potassium oxalate and the product, dried at 100°, had the composition Bi_2O_3 3 C_2O_3 4 H_2O. If this neutral oxalate be boiled repeatedly with water, a basic salt is formed to which various formulæ have been given — Bi_2O_3 2 C_2O_3 1½ H_2O (Heintz, Pogg, Ann. 63, 90) Bi_2O_3 2 $C_2O_3H_2O$ (Souchay and Lensson) and Bi_2O_3 2 C_2O_3 (Muir).

Owing to the easy decomposition of the neutral oxalate by water, I have not been able to obtain it entirely free from basic salt. This oxalate was used in a study of the basic oxalates similar to the researches by the author on the nitrates (Amer. Chem. Jour., 25, 307), and sulphates of bismuth (Amer. Chem. Jour., 27, 284). The salt was stirred with water and with oxalic acid solutions in a constant temperature bath. Owing to the length of time required to get equilibrium in monovariant systems, only divariant systems containing a gaseous, a liquid, and one solid phase have been obtained.

At 50° a basic salt, in which $\frac{Bi_2O_3}{C_2O_3}=3.23$, was found to be in equilibrium with oxalic acid solutions up to .085 normal and in stronger solutions the solid phase was the neutral salt. This basic salt was air-dried and analyzed, the bismuth being determined as the sulphide and the oxalic acid in the filtrate by titration with permanganate.

	Calculated for Bi_2O_3 2 $C_2O_3H_2O$	Found.
Bi_2O_3	74.16	74.14
C_2O_3	22.97	23.00
H_2O	2.87	(2.86)

Miller and Kenrick (Trans. Royal Soc. Canada, 1901), have shown that the number of possible phases in a given system is not changed if a new constituent be added to the liquid phase provided that this new constituent does not pass into the solid phase. This condition is

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fulfilled if dilute ammonia is stirred with Bi_2O_3 2 $C_2O_3H_2O$ and therefore a divariant system still contains but one solid phase. Preliminary experiments showed that the new basic salt obtained in this way was acted on by quite dilute ammonia and in order to get this solid phase in equilibrium with a larger range of concentrations of ammonia, it was necessary to reduce the efficiency of the ammonia in the reaction. This can be done by adding to the solution any ammonium salt, thus decreasing the amount of ionization and as ammonium oxalate is one of the products of the reaction it is the best salt for the purpose.

At 75°, Bi_2O_3 2 $C_2O_3H_2O$ was stirred with .028 normal ammonium oxalate and ammonia of varying concentrations and a new basic salt, in which $\frac{Bi_2O_3}{C_2O_3} = 9.69$, was found to be in equilibrium with ammonia solutions up to .115 normal. This salt when air-dried had the following composition:—

	Calculated for 3 Bi_2O_3 2 C_2O_3	Found.
Bi_2O_3	90.64	90.42
C_2O_3	9.36	9.47

When Bi_2O_3 2 $C_2O_3H_2O$ was stirred with stronger ammonia or potassium hydroxide, bismuth oxide was formed and there was no indication of the formation of another basic oxalate.

Souchay and Lensson have described the following double oxalates $Bi_2(C_2O_4)_3$ 7 $K_2C_2O_4$ 24 H_2O, $Bi_2(C_2O_4)_3$ 11 $K_2C_2O_4$ 24 H_2O and $Bi_2(C_2O_4)_3$ 15 $(NH_4)_2C_2O_4$ 24 H_2O.

They dissolved bismuth oxalate in concentrated hot solutions of the alkaline oxalates and the double salts crystallized on cooling the solutions. Results obtained by stirring bismuth oxalate with ammonium oxalate and with potassium oxalate threw doubt on the existence of these complex double salts and Souchay and Lensson's experiments have been repeated and the salts obtained were analyzed by Messrs. DeLury and Phillips.

A 4 per cent solution of ammonium oxalate was boiled with bismuth oxalate, using a reflux condensor, for half an hour, filtered hot, and the microscopic crystals formed on cooling were dried, under pressure, between paper. The ammonia was determined by boiling with potash and titrating the solution which distilled over.

	Calculated for $Bi_2(C_2O_4)_3(H_4)_2C_2O_4$ 8 H_2O	Found.
Bi_2	43.93	44.30
C_2O_4	37.08	36.85
NH_4	3.81	3.78
H_2O	15.18	(15.07)

The high value found for bismuth and the corresponding low values for oxalic acid and ammonia may be due to imperfect filtering or to a slight admixture of basic bismuth oxalate. This salt has not been previously described.

The preparation was then repeated using an ammonium oxalate solution saturated at 25° and the double salt obtained at 50° gave 3.85 per cent NH_4 and was identical with that previously analyzed. When this solution was cooled to room temperature two kinds of crystals were deposited which under the microscope were identified as this double salt and ammonium oxalate.

Bismuth oxalate was dissolved in a 20 per cent solution of potassium oxalate and the double salt obtained consisted of small white crystals. After the removal of the bismuth from the solution of the salt in hydrochloric acid the filtrate was evaporated and ignited and the potassium weighed as potassium chloride.

Calculated for $Bi_2(C_2O_4)_3 K_2C_2O_4 9\frac{1}{2} H_2O$		Found.
Bi	40.90	40.91
C_2O_4	34.56	34.54
K	7.69	7.69
H_2O	16.81	(16.86)

21 per cent and 23 per cent solutions of potassium oxalate gave the same double salt, but the deposit from a 26 per cent solution, at 50°, contained 36.1 per cent C_2O_4 and that from the same solution on cooling from 50° to room temperature contained 51.9 per cent C_2O_4 and these are probably mixtures of the double salt and potassium oxalate. Svensson (B, 3, 314)has described a double salt having the composition $Bi_2(C_2O_4)_3 K_2C_2O_4 2 H_2O$.

There is no evidence of the existence of the double salts described by Souchay and Lensson and the substances analyzed by them appear to have been mixtures.

In this paper three new componds have been described—3 Bi_2O_3 2 C_2O_3, $Bi_2(C_2O_4)_3 (NH_4)_2 C_2O_4 8 H_2O$ and $Bi_2(C_2O_4)_3 K_2C_2O_4 9\frac{1}{2} H_2O$.

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LABORATORIES

No. 47. THE ECONOMIC ADMISSION OF STEAM TO WATER-GAS PRODUCERS OF THE LOWE TYPE.

BY C. M. WEEKS.

Bulletin issued by the Bureau of Soils, Milton Whitney, Chief of Bureau.

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THE ECONOMIC ADMISSION OF STEAM TO WATER-GAS PRODUCERS OF THE LOWE TYPE.

BY G. W. McKEE.

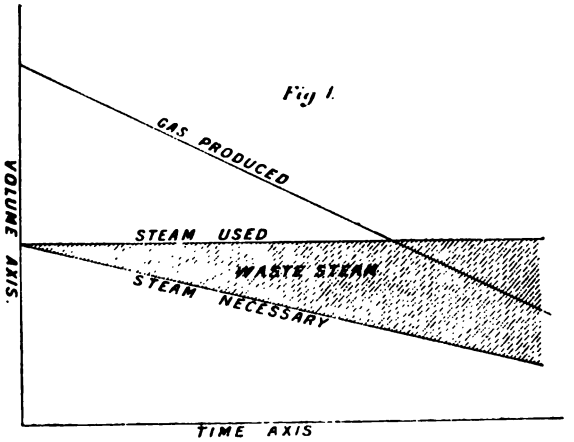
It is the general practice of water-gas operators to vary the quantity of steam admitted according to the conditions of the producer, these conditions being:—(1) Temperature in the generator judged by the length of the preceding "blow." (2) Depth of the fuel bed. (3) The question as to whether an up or down run is being made. (4) The length of time that has expired since clinkering. The amount of steam admitted is judged by the number of turns given to the valve, sometimes checking the working of the steam line by an observation of the nozzle pressure, taken from a Bourdon's gauge placed on the wall. The important point to which it is desired to call attention is that in every case the steam valve is left open the same amount during the whole run.

If we consider the reaction for the formation of water-gas, *viz.*—

$$\underset{\text{1 vol.}}{C} + \underset{\text{1 vol.}}{H_2O} = \underset{\text{1 vol.}}{CO} + \underset{\text{1 vol.}}{H_2}$$

we have one volume of steam yielding two volumes of gas. Of course, above 1200° C. the reaction is complicated by the fact that hydrogen acts directly on carbon, forming CH_4, C_2H_6, C_2H_2, &c.; but, since the percentages of these gases in water are small, we may, for the purposes of the following argument, leave them out of consideration. Of two things we are sure, *viz.*: (1) the volume of steam used should, at corrected temperature and pressure, be approximately one half that of the gas produced; (2) if any undecomposed steam gets through the machine we are not running up to the highest efficiency; for (*a*) it is costly to produce the steam in the boiler room; (*b*) the surplus steam passing through the generator has to be raised to the heat of the coke, and this heat is abstracted from the machine; (*c*) this steam must again be condensed in the condensers, thus necessitating the pumping of extra condenser water; (*d*) furthermore, the following reaction, $H_2O + CO = CO_2 + H_2$, is liable to be set up in the space above the coke, and in the carburetter and superheater settings. This reaction begins at 625° C., and comes to an equilibrium which is in accordance with the temperature prevailing in the machine.

The experiments which follow were conducted in three water-gas machines, two of them being those of the United



Gas Improvement Company, and the third of the Western Gas Construction Company of Indiana. The length of blow was six minutes, and the length of run eight minutes. In the first place it was observed from the scale-board in the operating room that by far the greater portion of the gas made during the run was obtained in the first three or four minutes. A ¼-in. pet-cock was then attached to the superheater of one of the machines, and a "dry run" was made. A thin-walled glass Leibig condenser was attached to the pet-cock, and it was found possible to condense water out of the gas at the latter part of the eight-minute period. Comparing, then, the gas produced and the quantity of steam employed, Fig. 1 may be expected to represent the condition of affairs.

In order to accurately determine the amount of gas produced at short intervals, and to establish a curve on the lines indicated above, various devices were tried, including Pictet's meter, but the best results were obtained by a direct measurement of the rate from the relief holder. A long rod, A (Fig. 1), was suspended from the railing that went up and down with the relief holder by means of a strap iron hook. At intervals of about 30 c.m., gimlet holes were made in this rod. A second rod, B, of the same dimensions as the above was made, and pointed at one end. The other end was secured to a heavy wooden block placed on the stone coping of the gasometer, and held in place by weights. A third strip, C, was prepared, with a thumb-screw in one end, and strips of heavy paper secured to it by means of tacks. In this way the rod C could be quickly fastened to A in such a way that the upper part of the strip of paper on C would be level with the bevelled

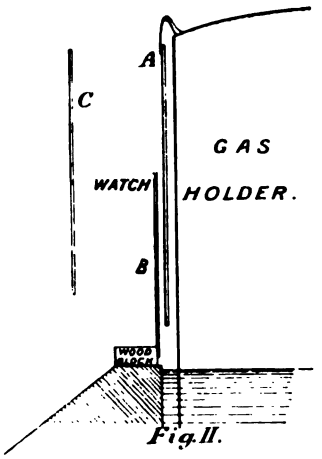
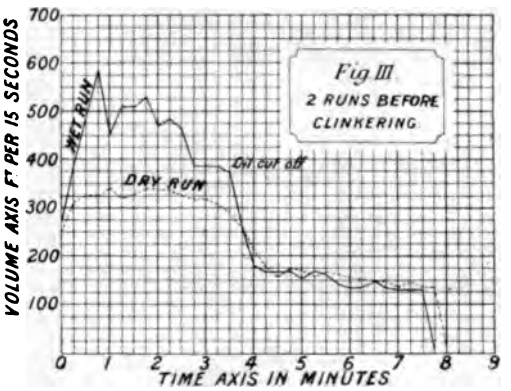
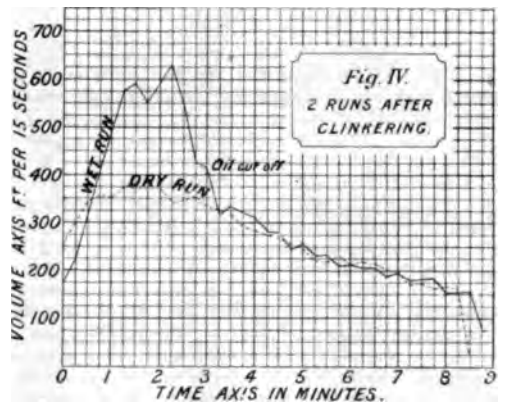


Fig. II.

point of B. A small hook was screwed in B at the point indicated, and a watch hung on it. All the water-gas machines except one were stopped, and the exhauster pumping from the holder was also stopped. When the machine began "the run" the holder would begin to rise, and, every 15 minutes, marks were made on the strip of paper opposite the point of B. The strips of wood were sufficiently thin to permit of them all being grasped in the left hand at once, and so the above markings could be quickly and accurately made. These measurements were continued over several days with both "dry" and "wet" runs. The best curves were obtained on calm days, as the slight movements of the holder caused by wind showed in the curves which were subsequently plotted. It was also found possible to obtain fairly good curves with the exhauster running by having the engineer maintain it at a constant rate, and by noting the rate from a slip of paper both before and after "the run." Very accurate measurements were taken of the capacity of the holders, and a table prepared for convenience in calculation. The distances between the marks on the strip of paper were transferred to a finely-divided rule with dividers, thus giving the number of inches between the markings, and by consulting the table this was readily transferred to cubic feet of gas produced per 15 seconds. In the curves produced we have nearly one minute consumed in reaching the maximum rate of output. This is accounted for by the following facts:—(1) The initial fraction is cooled below its average temperature on entering the condenser. (2) In the case of a wet run a certain amount of time is used up in admitting the oil, the inflow of





which gradually rises to a maximum. (3) The mains and the gas already in the holder is further removed from the temperature of the first fraction of the gas than from that formed in the succeeding part of the run. For these reasons the true curve of make conditioned by the internal state of the generator should, without doubt, be parallel to the time axis. This fact would tend to increase the output of the first three minutes above that shown in the curves actually obtained, and, *ipsa causa*, decrease the output of the latter part of the run. This would be an added argument for the method of operating proposed later on.

From the curves shown it is apparent that the curve falls off enormously between the third and fifth minute in every

case, which is about the time that the oil is cut off in the production of a gas of from 18 to 25 c.p. It would seem to be well, then, to cut the steam supply down to one half directly after cutting off the oil supply. This would be in accord with the convenience of the men in operating the machines. Furthermore, it would be approximately correct, and would allow the machine to have its full capacity during the beginning of the run, thus securing the maximum daily output. This being settled upon, it becomes of importance to know just how much steam passes the inlet valve, and how much it is necessary to close the valve to cut that supply down to one half. A series of experiments were done on globe valves to determine the above, and it was established beyond a doubt that no simple relation exists between the number of turns a globe valve is opened and the amount of steam which passes in a given time. Some better control of the steam is evidently necessary. This is to be found in the nozzle pressure appliances which are attached to most water-gas machines. Rankin, after a consideration of Napier's work on the subject, gives the following empirical formula for the amount of saturated steam escaping from a chamber where the pressure is p, through a short pipe and nozzle into a space where the pressure is p_a :—

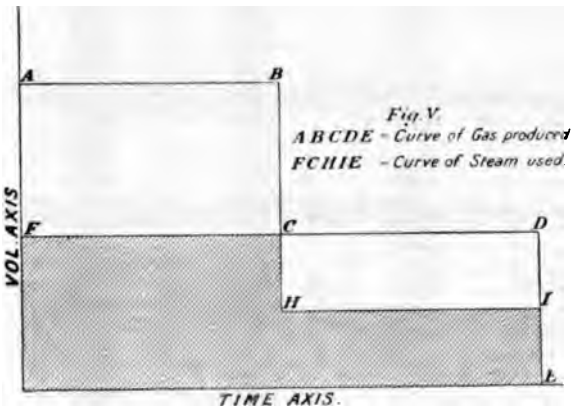
(1) Where p = or > $\frac{5}{8} p_a$, $w = \frac{ap}{70}$.

(2) Where $p < \frac{5}{8} p_a$, $w = \frac{a\, p^a}{42} \left(3\,\frac{(p-p_a)}{2\,p_a}\right)^{\frac{1}{2}}$.

In the above formula w = the number of pounds of steam delivered per second, and a is the area of the orifice in square inches. In water-gas practice conditions are somewhat different from the experiments on which the above formulæ were established, insomuch as we have a long steam line, and take the nozzle pressure, not from the boiler, but between the steam valve and the nozzle, at a point past which the steam is moving rapidly. If we apply the above formula, taking p as the indicated nozzle pressure, then p = 30 to 40 lb. per square inch, while p_a is measured in a few inches water pressure, and the first formula applies; from which it follows that the amount of steam delivered in a given time varies directly with the nozzle pressure, and also directly with the area of the orifice. A series of experiments testing the accuracy of the above formula under water-gas conditions would be interesting.

Conclusions.—From actual experiments carried out, extending over more than a month, in which the nozzle pressure was cut down by one half after the fourth minute, a considerable saving in coke was effected, and the composition of the gas was in a measure modified also, its carbo-dioxide contents being lowered. Under this system of working the gas and steam curves would resemble Fig. 5,

though a curve of this kind was not actually taken from the machines. The above remarks apply where gas-coke



is used in the generators; modifications may be expected in the case where anthracite coal is employed. From the curves just after clinkering, it is apparent that the machine's capacity could be increased by dividing the blow into three periods, and cutting the steam down to one-third each time. It being possible, therefore, to approximately regulate the amount of steam admitted during the run in accordance with the curves obtained, the yield of gas is increased, and the machine can be run up to its highest efficiency owing to the fact that the conditions causing imperfect working, indicated under (*a*), (*b*), &c., no longer exist.

The author wishes to acknowledge his indebtedness to Prof. W. R. Lang, of the University of Toronto, for the advice and assistance rendered in collating his experimental results.

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THE RATE OF FORMATION OF IODATES IN ALKALINE SOLUTIONS OF IODINE

BY E. L. C. FORSTER

Up to the year 1861, in which Schönbein's "*Beiträge zur nähern Kenntniss des Sauerstoffs und der einfachen Salzbildner*"[1] appeared, it was generally believed that iodine and caustic potash in solution react instantaneously to form potassium iodate. Schönbein showed that the reaction takes place in two ostges, and, relying on the close analogy between the chemical behaviour of iodine and chlorine, assumed that the intermediate product was potassium hypoiodite.

With regard to the first stage — formation of hypoiodite — his experiments show that the reaction is incomplete and reveraible, leading to an equilibrium between potash, iodine, iodide and hypoiodite; with regard to the second — formation of iodate — which differs from the first in requiring a measurable time for its completion, Schönbein says little, merely pointing sut that rise in temperature increases the rate.

In 1894 there appeared a paper by Lonnes[2] containing measurements of the amount of iodate formed in solutions of iodine and sodium carbonate at measured intervals of time, which show that the rate of the reaction is influenced by the concentrations of the iodide and of the alkali; and in the following year Schwicker[3] — in the only formal study of the "rate of transformation of potassium hypoiodite" that has as yet appeared — found that the rate was proportional to the square of the concentration of the "iodine," and that increase in the quantity of potash caused a retardation almost proportional to the excess of KOH over that needed to form hypoiodite. In a few experiments in which the iodine was present in slight excess,

[1] Jour. für prakt. Chem. 84, 385 (1861).
[2] Zeit. anal. Chem. 33, 409 (1894).
[3] Zeit. phys. Chem. 16, 303 (1895).

the rate was thought to be proportional to the cube of the concentration of the iodine; no account was taken of the influence of the potassium iodide.

In the opinion of Taylor,[1] Schwicker's results "do not appear to have been altogether satisfactory;" this he ascribes to that author's neglect of the effect due to the potassium iodide in his "iodine" solution. That the rate is in reality largely dependent on the concentration of the iodide, was again shown by Förster and Gyr[2] in a paper on "the action of iodine on alkalis," published in January of the present year.

In the experiments described in the present paper, I have examined the effect of changing the quantities of potash, iodine, and potassium iodide, on the rate of formation of potassium iodate in alkaline solutions of iodine. When the potash is present in large excess — colourless solutions — the results are simple, and can be expressed with a fair degree of accuracy by saying that the rate is proportional to the concentration of the iodion $\bar{I}$, the hypoiodion $\overline{OI}$, and the hypoiodous acid HOI. In brown solutions, on the other hand, where the iodine is in excess, the relations are more complex; and, until the numerical values of certain constants have been determined, it cannot be asserted that the laws suggested by the experiments with colourless solutions are valid for all.

My measurements show that Förster's equation

$$KOI + 2HOI = KIO_3 + 2HI,$$

which in that author's opinion "corresponds in all details" with the reaction itself, must be rejected equally with the older theory adopted by Schwicker and others

$$3KOI = KIO_3 + 2KI,$$

and that in all probability it must be replaced by some equation of which the left member is

$$(?\ H_2O +)\overline{OI} + HOI + \bar{I},$$

[1] Chem. News, 76, 17 (1897).

[2] Zeit. Elektrochemie, 9, 1 (1903).

and of which the right can be filled in, for the present, only by a draft on the imagination.

I. Colourless Solutions

The solution of potash was mixed with the water in a 400 cc Erlenmeyer flask and brought to zero by immersion in a well-stirred bath of ice and water; the mixed solutions of iodine and potassium iodide, also at zero, were then quickly poured in, the whole well shaken and the time noted. After two minutes the first analysis was made; 10 cc was pipetted into a mixture of 50 cc water with 20 cc of a half-saturated solution of ammonium bicarbonate, by which further formation of iodate was prevented, and the residual "iodine" (hypoiodite) was then determined by *n*/100 sodium arsenite with starch as indicator, 0.5 cc *F*[1]-*KI* being added to make the end-point distinct; *n*/100 iodine was used to "titrate back", and a correction of 0.1 cc was applied to the reading, being the amount of iodine needed to give the blue colour.

The stock solutions used in all the experiments described in this paper, with the exception of those of Tables XIII and XIV were: 1.092-normal potash, freed from carbonate by lime, 1.151-*F* potassium iodide, and 0.0936-normal iodine, the latter being prepared by dissolving about 12.7 grams of iodine in 100 cc of the 1.151-*FKI* and diluting to a liter. They were standardized in the usual manner, with sulphuric acid, silver, and sublimed iodine respectively. The volumetric solution of sodium arsenite was 0.01025-normal (against iodine) and the thiosulphate was 0.0104-normal (against the arsenite).

The potassium iodide employed contained small quantities of potassium iodate and potassium carbonate; these were removed by acidifying with sulphuric acid, boiling to expel CO_2, adding sodium thiosulphate until the solution just gave no blue with starch, and finally neutralizing with caustic potash freed from carbonate by lime. The water used in making up the reacting mixtures was freed from CO_2 by boiling for fifteen minutes, and was protected by soda lime.

[1] One formula-weight in grams per liter.

The pipettes were calibrated by weighing the distilled water discharged; 30 seconds being allowed for draining.

At the head of each table is given the volume of each of these stock solutions employed. Under θ is entered the time in minutes reckoned from the first analysis (for which $\theta = 0$); under As, the number of cc of the volumetric arsenite solution required to remove the iodine in 10 cc of the reacting mixture, and under $K_2 \times 10^4$ the value of $10^4(1/As - 1/As_0) \times 1/\theta$.

Adopting Schönbein's assumption, that when iodine is dissolved in a solution of potash, potassium hypoiodite is formed, the quantities of the constituents $\overline{OH}$, $\bar{I}$, and $\overline{OI}$ may be determined by means of the equation

$$2\overline{OH} + \bar{I}_3 = \overline{IO} + 2\bar{I} + H_2O,$$

the quantity of $\bar{I}_3$ in colourless solutions obviously being zero.

Let A, B, and C represent the numbers of gram-molecules of KOH, KI, and KI_3 before mixing, multiplied in each case by 10^5. Thus for example, in Expt. 1:

50 cc potash: $A = 10^5 \times 0.050 \times 1.092 = 5460$
20 cc iodine: In making this up there was used
$10^5 \times 0.020 \times 0.1151$ units of potassium iodide, of which
$10^5 \times 0.020 \times 0.0936 \times 0.5 = 93.6 = C$ was converted into KI_3, leaving
$10^5 \times 0.020 \times 0.0683 = 136.6$ KI
20 cc iodide: containing $10^5 \times 0.020 \times 1.151 = 2302$ KI, to which must be added 136.6 in the iodine solution, giving $2439 = B$.

Then after mixing, when all the triiodion, $\bar{I}_3$, has been converted into hypoiodion, $\overline{OI}$, but before the formation of iodate has commenced,

the $\overline{OH}$ present $= A - 2C = 5560 - 187 = 5273$
" $\bar{I}$ " $= B + 2C = 2439 + 187 = 2626$
" $\overline{OI}$ " $= C = 94.6$

In the calculation it has been assumed that, owing to the

large excess of potash, the concentration of the HOI might be neglected in comparison with that of the $\overline{OI}$ ions.

In addition to the experiments recorded in the tables, others were carried out which showed that the presence of a small quantity of potassium iodate (one gram in 100 cc) has no effect on the rate, and that the possible absorption of carbonic acid from the air during the progress of an experiment was likewise without influence on the result. In a few measurements the reacting mixture was exposed to direct sunlight; the same figures were obtained as in duplicates made in the diffuse light of the laboratory.

In Table VI, the initial compositions of the solutions in the experiments of Tables I to V are given in the terms of $\overline{OH}$, $\bar{I}$, and $\overline{IO}$, together with the average values of K_2. The initial rate, R_0, is obtained by multiplying K_2 into the square of the initial concentration of the hypoiodion,

$$R_0 = dx/d\theta(x=o) = K_2C^2.$$

From the constancy of K_2 in each of the Tables I–V, it is apparent that the rate is proportional to the square of the concentration of the $\overline{OI}$; this conclusion is confirmed (within 10 percent) by comparison of Tables I and II (see also Table VI).

TABLE I.

Potash, 50 cc; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	9.06	—
3	8.52	23.3
10	7.54	22.2
15	7.24	25.1
19	6.40	24.1
22	5.99	25.6
		Av. 24.1

TABLE II.

Potash, 50 cc ; Iodide, 20 cc ; Iodine, 40 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	17.25	—
4	14.70	25.1
9	11.77	29.9
13	10.06	31.8
17	8.68	33.6
22	7.53	34.0
27	7.27	29.4
		Av. 30.6

TABLE III.

Potash, 100 cc ; Iodide, 20 cc ; Iodine, 20 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	8.75	—
4	8.37	13.2
8	8.18	10.0
12	7.62	14.1
16	7.60	10.9
20	7.09	13.4
24	6.93	13.9
		Av. 12.5

TABLE IV.

Potash, 25 cc ; Iodide, 20 cc ; Iodine, 20 cc ; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	9.09	—
4	7.95	39.5
8	6.80	46.2
18	5.08	48.0
22	4.50	55.0
26	4.00	53.8
		Av. 48.5

TABLE V.

Potash, 50 cc; Iodide, 10 cc; Iodine, 20 cc; Volume, 200 cc

θ	As	$K_2 \times 10^4$
0	8.95	—
6	8.48	10.3
9	8.27	10.2
13	7.88	11.6
17	7.25	15.4
		Av. 11.8

TABLE VI.

Table	$\overline{OH}$	$\bar{I}$	$\overline{OI}$	$K_2 \times 10^4$	R_0	$K^1 \times 10^4$
1	5273	2626	93.6	24.1	21.1	47
2	5086	3050	187.2	30.6	107.3	51
3	10733	2626	93.6	12.5	11.0	50
4	2543	2626	93.6	48.5	42.5	46
5	5273	1475	93.6	11.9	10.4	43

Further comparison of the experiments, which is facilitated by the summary given in Table VI, shows that within the same limits (8 to 10 percent) the rate is directly proportional to the concentration of the $\bar{I}$, and inversely to that of the $\overline{OH}$. Since the product of $\overset{+}{H}$ and $\overline{OH}$ concentrations is constant, and since the concentration of the HOI is proportional to the product of those of $\overset{+}{H}$ and $\overline{OI}$, this is equivalent to saying that the rate is proportional to the concentrations of $\overline{OI}$, $\bar{I}$, and HOI.

II. Brown Solutions

In presence of a large excess of iodine, the plan of analysis described on page 642 would give very inaccurate results; it was therefore abandoned in favor of a direct determination of the iodate formed, according to the following method.

The iodine and hypoiodite were destroyed and the reaction stopped by pouring in a slight excess of fifth-normal sodium arsenite. The contents of the flask were then emptied into a beaker, 100 cc of water added, and then a measured quantity of

[1] $Ro \times (OH) = K \times (I) \times (OI)^2$

hydrochloric acid diluted with 100 cc of water; the iodine which was thereupon liberated from the iodate was determined by sodium thiosulphate. Under x in the tables of this section is entered the number cc of 0.0104-n thiosulphate needed, and under θ the interval in minutes between mixing the reagents and adding the arsenite. By working quickly, using as little arsenite as possible, and adding in each case a definite excess (5 cc of 2-n HCl) of hydrochloric acid over that needed to neutralize the potash in the reacting mixture and the sodium bicarbonate in the arsenite solution, it was found possible to determine the iodate before any iodine was liberated by arsenic acid. It would have been better to remove the excess of arsenite before acidifying, but blank experiments show that the error arising from its presence is small.

A series of experiments analogous to those of Tables I–V were first carried out, but as no "constant" could be found, recourse was had to the "method of constant rates,"[1] the solutions being so made up that the changes in concentration during the progress of an experiment were almost negligible. In Tables VII–XII the rates (R) were obtained by dividing x (which is proportional to the amount of iodate formed) by the duration of the reaction in minutes. Duplicate experiments showed that the value of R so obtained was rather greater when θ was 3 or 4 minutes than when it was one; this suggests that the formation of hypoiodite may require an appreciable interval of time for its completion, but I have not examined the matter further.

TABLE VII.

Potash varies; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
1	Brown	2	2.1
2	Brown	1	11.3
5	Light brown	1	8.7
10	Green yellow	1	4.2
15	Light green	2	2.9
20	" "	4	2.1
25	" "	5	1.6

[1] See Bray, Jour. Phys. Chem. 7, 92 (1903).

TABLE VIII.

Potash varies; Iodide, 40 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
2	Brown	1	4.2
5	Yellow brown	1	11.1
10	Yellow green	1	9.3
15	Green yellow	1	6.0
20	" "	1	3.8
25	" "	3	3.4

TABLE IX.

Potash varies; Iodide, 60 cc; Iodine, 20 cc; Volume, 200 cc

KOH	Color	θ	R
2	Brown	4	1.9
5	"	1	8.4
10	"	1	11.6
15	Yellow brown	1	10.7
20	Yellow green	1	6.4
25	Green yellow	1	5.0

TABLE X.

Potash varies; Iodide, 20 cc; Iodine, 40 cc; Volume, 200 cc

KOH	θ	x	R
1	2	10.6	5.3
2	1	22.9	22.9
3	1	44.1	44.1

TABLE XI.

Potash varies; Iodide, 40 cc; Iodine, 40 cc; Volume, 200 cc

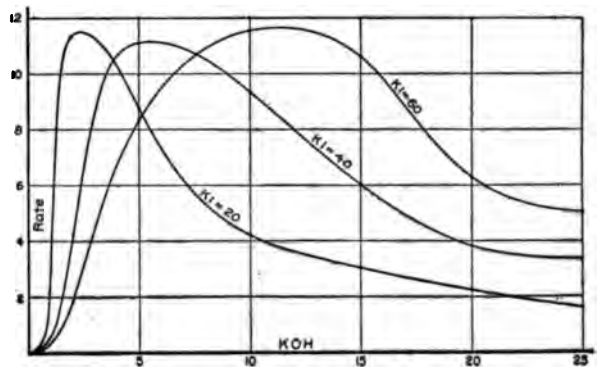
KOH	θ	x	R
1	2	3.3	1.6
2	1	9.6	9.6
3	1	23.1	23.1

TABLE XII.

Potash varies; Iodide, 60 cc; Iodine, 40 cc; Volume, 200 cc

KOH	θ	x	R
1	3	2.2	0.7
2	1	4.5	4.5
3	1	12.3	12.3

From Tables VII–XII it appears that, in presence of a large excess of iodine, the rate of formation of iodate is increased by increasing the concentration of the iodine or of the potash, and decreased by increasing that of the iodide — the effect in the last two cases being the opposite of that produced when the potash is in excess. The existence of maximum rates, which is necessitated by this circumstance, is well shown by the curves.



Tables 7, 8, and 9

It would be interesting to know whether in the experiments of this section, as in those with colorless solutions, the rate is even roughly proportional to the concentrations of $\overline{OI}$, $\bar{I}$, and $\overline{HOI}$; in brown solutions, however, where only part of the iodine is converted into hypoiodites, it is not easy to determine the amounts of these three constituents.

Assuming the chemical equations: —

$$\overset{+}{H} + \overline{OH} \rightleftarrows H_2O$$

$$\overset{+}{H} + \overline{OI} \rightleftarrows HOI$$

$$\overline{OH} + \bar{I}_3 \rightleftarrows HOI + 2\bar{I},$$

and the corresponding conditions of equilibrium:—

$$(\overset{+}{H})\,(\overline{OH}) = W$$
$$(\overset{+}{H})\,(\overline{OI}) = D(HOI)$$
$$(\overline{OH})\,(\bar{I}_3) = E\,(HOI)\,(\bar{I})^3,$$

(where the symbols in brackets signify the amounts of the reagents in a fixed volume of solution, and W, D, and E are constants) and representing the initial quantities of potash, iodide, and iodine by A, B, and C as before, the following equations

$$Wy = Dz(A - 2y - z)$$
$$(A - 2y - z)\,(C - y - z) = Ez(B + 2y + 2z)^3,$$

determining y, the concentration of the $\overline{OI}$ ions, and z that of undissociated HOI (before the formation of $\overline{IO_3}$ has begun) may be obtained. These equations may be solved for y and z, and the results substituted in the expression for the rate of formation of iodate,

$$R = Kyz\,(B + 2y + 2z),$$

but without knowledge of the numerical values of D and E the relation so obtained cannot be compared directly with the experiments. I hope to determine these constants during the present winter; in the meantime the experiments of this section, though perhaps not so accurate as those in which the potash was in excess, and not leading to such simple results, serve to show how much the brown solutions differ from the colourless in respect to the influence exerted by the amounts of iodide and of potash on the rate of formation of potassium iodide.

Temperature Coefficient

A few experiments were undertaken at 30.3° in order to test the influence of the temperature on the rate; those with the colourless solutions are given in Table XIII, and those with brown solutions in Table XIV. In neither case is the temperature coefficient as great as usual, but as in all probability the dissociation of HOI and the equilibrium constant E (see above) change with the temperature, abnormal results are not to

be wondered at. The experiments of Table XIII were carried out with solutions of potassium iodide that had not been freed from carbonate, and are therefore not directly comparable with the other experiments of this paper.

TABLE XIII. (Colourless)

Potash, 25 cc (0.929-n); Iodide, 20 cc (0.956-F); Iodine 20 cc (0.089-n); As (0.0101-n) Volume, 200 cc

θ	As(0°)	$K_2 \times 10^4$(0°)	As(30.4°)	$K_2 \times 10^4$(30.4°)
0	—	—	6.28	457.0
7	6.78	45.0	2.32	396.8
10	6.32	40.6	1.68	437.9
14	5.56	44.3	—	—
20	4.80	45.1	—	—
		Av. 43.7		Av. 431.

TABLE XIV. (Brown)

Potash, 1.0 cc; Iodide, 20 cc; Iodine, 20 cc; Volume, 200 cc

θ	x	R(0°)	θ	x	R(30.3°)
2	4.2	2.1	1	32.3	32.3

Summary

In the presence of a large excess of potash, the rate of formation of potassium iodate is, approximately, proportional to the concentrations of $\overline{OI}$, $\bar{I}$, and HOI.

In presence of a large excess of iodine, the rate is increased by increasing the amount of potash or iodine, and decreased by adding to that of the potassium iodide.

On continually increasing the amount of potash, so that the solution changes from brown to colourless, the rate passes through a maximum.

The temperature coefficient is smaller than is customary.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this investigation was undertaken, and under whose supervision it has been carried out.

University of Toronto,
October, 1903.

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NUMERICAL VALUES OF CERTAIN FUNCTIONS INVOLVING e^{-x}

Owing to defective type, some figures in the following decimals are not distinct.

Page 83,	$x=.173$,	second integral	.343 044 342
" 87,	" .379,	fifth "	.986 305 616
" 89,	" .457,	fifth "	.977 326 592
" 89,	" .486,	fifth "	.973 302 994
" 89,	" .494,	first "	.668 065 730
" 91,	" .555,	fourth "	.892 682 366
" 93,	" .676,	second "	.391 304 134
" 95,	" .793,	first "	.256 039 989
" 107,	" 1.23,	.237 636 242	

ERRATA

Page 73 and 74, Eqns. 6, 7, 8, 9, *for* K *read* K q^{1-a}

" 80, footline, *for* $\int \frac{e^{-x}}{x^2} dx$ *read* $\int_x^\infty \frac{e^{-x}}{x^2} dx$

" 80. $x=.001$, third integral *for* .999 000 500 *read* 0.999 000 500

" 80, $x=.001$, fourth " " .999 999 500 " 0.999 999 500

" 100, $x=1.31$, fourth " " .632 284 330 " .623 284 330

" 106, $x=.910$, *for* .442 334 314 *read* .442 334 312

X.—*Numerical values of certain functions involving* e^{-x}.

By W. LASH MILLER, Ph.D., and T. R. ROSEBRUGH, M.A.

(Read May 19, 1903.)

In dealing with certain problems of Chemical Kinetics,[1] equations of the form

$$k\,du = \frac{dz}{(A-z)^{\alpha}(B-z)^{\beta}(C-z)^{\gamma}\ldots} \tag{1}$$

are commonly met with. The tables published herewith were first computed (to a less number of decimal places) in order to furnish a ready means of integrating them.

In Equation (1), A, B, C, . . are positive constants, arranged in order of magnitude, A being the smallest; α, β, γ, . . are any real quantities; and z may range from 0 to any value less than A.

In Equation (1) making the substitution

$$Ay = A - z, \tag{2}$$

there follows

$$K\,du = \frac{-dy}{y^{\alpha}(1+by)^{\beta}(1+cy)^{\gamma}\ldots} \tag{3}$$

in which

$$b = \frac{A}{B-A},\quad c = \frac{A}{C-A},\ \text{etc.}$$

$$K = k\,A^{\alpha-1}(B-A)^{\beta}(C-A)^{\gamma}\ldots$$

Equation (3) may be written

$$K\,du = \frac{-dy}{y^{\alpha}} \cdot e^{-qy+ry^2-sy^3+ty^4-\ldots} \tag{4}$$

where $q = \Sigma\beta b$, $r = \frac{1}{2}\Sigma\beta b^2$, $s = \frac{1}{3}\Sigma\beta b^3$, $t = \frac{1}{4}\Sigma\beta b^4$.

If b, c, . . , are small (y being obviously less than unity), the series in the exponent of e converges rapidly, and Equation (4) may be (approximately) replaced by

$$K\,du = \frac{-dy}{y^{\alpha}} \cdot e^{-qy}(1 + ry^2 + \tfrac{1}{2}r^2y^4 - sy^3 + ty^4) \tag{5}$$

Writing x for qy and integrating (with the lower limit $u = 0$, $z = 0$)

$Ku =$

$$-\int e^{-x}x^{-\alpha}\,dx - \frac{r}{q^2}\int e^{-x}x^{2-\alpha}\,dx + \frac{s}{q^3}\int e^{-x}x^{3-\alpha}dx - \frac{t+\frac{1}{2}r^2}{q^4}\int e^{-x}x^{4-\alpha}dx \tag{6}$$

[1] The subject is more fully discussed in a paper which will shortly be published under the title: T. R. Rosebrugh and W. Lash Miller—A convenient integral form of the Equations of Chemical Kinetics.

The cases where $\alpha = 0$, $\alpha = 1$, and $\alpha = 2$, are of particular importance in the class of problems already referred to. Introducing these values Equation (6) becomes[1]

$$\alpha = 0,\ Ku = -\int e^{-x}dx - \frac{r}{q^2}\int e^{-x}\,x^2\,dx \tag{7}$$

$$\alpha = 1,\ Ku = -\int \frac{e^{-x}}{x}\,dx - \frac{r}{q^2}\int e^{-x}\,x\,dx + \frac{s}{q^3}\int e^{-x}\,x^2\,dx \tag{8}$$

$$\alpha = 2,\ Ku = -\int \frac{e^{-x}}{x^2}\,dx - \frac{r}{q^2}\int e^{-x}\,dx + \frac{s}{q^3}\int e^{-x}\,x\,dx - \frac{t + \frac{1}{2}r^2}{q^4}\int e^{-x}\,x^2\,dx \tag{9}$$

and by means of tables of these integrals computations can be carried out with much less labour than if the method of integration by partial fractions —assuming its applicability—were employed. This is particularly the case when the factors in Equation (1) are numerous, or the exponents large.

The most general form of Equation (1) may be written

$$K\,du = \frac{-\,dy}{y^{\alpha}\,(1 + g_1y + h_1y^2 + m_1y^3 + \ldots)^{\beta}\,(1 + g_2y + h_2y^2 + m_2y^3 + \ldots)^{\gamma}\ldots}$$

from which the following values of q, r, s . . . . may be found

$$q = \Sigma\beta g\,;\ r = \tfrac{1}{2}\,\Sigma\beta g^2 - \Sigma\beta h\,;\ s = \tfrac{1}{3}\,\Sigma\beta g^3 - \Sigma\beta gh + \Sigma\beta m$$

As β, γ . . . may be negative, this form includes the cases where factors are contained in the numerator as well as in the denominator. When the indices are fractional, the method here described affords a means of integration where others fail; it is, however, as already stated,

[1] If e^x be substituted for e^{-x}, the sign of the variable limit must be reversed, and that of the integral may be affected. Thus:

$$\int_{-x}^{-\infty}\frac{e^x}{x^2}dx = -\int_{x}^{\infty}\frac{e^{-x}}{x^2}dx$$

$$\int_{-x}^{-\infty}\frac{e^x}{x}\,dx = \int_{x}^{\infty}\frac{e^{-x}}{x}dx$$

$$\int_{-x}^{-\infty}e^x\,dx = -\int_{x}^{\infty}e^{-x}\,dx$$

$$\int_{-x}^{-\infty}e^x\,x\,dx = \int_{x}^{\infty}e^{-x}x\,dx$$

$$\int_{-x}^{-\infty}e^x x^3dx = -\int_{x}^{\infty}e^{-x}x^3dx$$

subject to the limitation that the series in the exponent of e must converge rapidly.

Of the integrals

$$\int \frac{e^{-x}}{x^2}\,dx, \int \frac{e^{-x}}{x}\,dx, \int e^{-x}\,dx, \int xe^{-x}\,dx, \int x^2e^{-x}\,dx,$$

The first may be reduced to the second, the so-called "Exponential Integral" $Ei(-x)$, and the fourth and fifth to the third, or Exponential Function.

The Exponential Function has been tabulated by Mr. F. W. Newman,[1] from $x = 0$ to $x = 37$, at intervals of .1 to eighteen decimal places (sixteen exact), from $x = 0$ to $x = 15.349$ at intervals of .001 to twelve decimal places, from $x = 15.350$ to $x = 17.298$ at intervals of .002, and from $x = 17.300$ to $x = 27.635$ at intervals of .005 to fourteen decimal places.

Tables of the same function have been prepared by Mr. J. W. L. Glaisher[2] from $x = 0.001$ to $x = 1.000$ at intervals of .001, from $x = 0.01$ to $x = 2.00$ at intervals of .01, from $x = 0.1$ to $x = 10.0$ at intervals of .1, and from $x = 1$ to $x = 500$ at intervals of unity. In every case the first nine significant figures are given.

The Exponential Integral has been tabulated by Mr. J. W. L. Glaisher[3] from $x = 0$ to $x = 1.00$ at intervals of .01 to eighteen places, from 1.0 to 5.0 at intervals of .1 to eleven places, and from 6.0 to 15.0 at intervals of unity to eleven places.

For the problems with which we were concerned, these intervals were too wide, we have therefore constructed a table of the descending Exponential Integral from $x = 0$ to $x = 1.000$ at intervals of .001, and from $x = 1.00$ to $x = 2.00$ at intervals of .01, to nine decimal places.

The other three integrals have not hitherto been tabulated, so far as we are aware.

Values of $\int_x^\infty e^{-x}\,dx$, *from* $x = 0$ *to* $x = 1.000$ *at intervals of* .001 (*Table I*), *and from* $x = 1.00$ *to* $x = 2.00$ *at intervals of* .01 (*Table II*). These are Newman's values of e^{-x} to the nearest digit in the ninth decimal place.

In his "Tables of the Exponential Function" Glaisher says: "The last figure is therefore in general correctly given to the nearest unit, but it may be in error by a unit where the tenth figure is a 4, 5 or 6." On comparing Glaisher's table with that of Newman five cases were found

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[1] Cambridge Phil. Trans., XIII, 145 (1883).

[2] *Ibid*, XIII, 243.

[3] Phil. Trans., CLX, 367 (1870).

between $x = 0$ and $x = 2$ (viz., $x = 0.820$, 1.28, 1.75, 1.93, 1.99) in which there was a discrepancy of one unit in the ninth decimal place, and the tenth digit was 4 or 5.

There are two others in which the tenth figures are 2 and 8 respectively, viz.:

x	Newman	Glaisher
1.55	0.212 247 973 827	0.212 247 973
1.80	0.165 298 888 221	0.165 298 889

In both cases Newman's result was found to be exactly the square of his number for half the value of x.

Values of $\frac{e^{-x}}{x}$, *from* $x=0.100$ *to* $x=1.000$ *at intervals of* .001 (*Table III*), *and from* $x = 1.00$ *to* $x = 2.00$ *at intervals of* .01 (*Table IV*). These were obtained by division from Newman's values of e^{-x}.

For use in calculating the Exponential Integral the first, second and following differences of the first seven decimal places were taken until they were small enough to be followed readily, these served also to detect errors in the first six places. At the beginning of the table, $x = 0.100$ to $x = 0.210$, the differencing was extended to the whole nine decimal places.

The last six figures of $\frac{e^{-x}}{x}$ were then multiplied by the corresponding value of x and the product compared with Newman's value of e^{-x}, thus eliminating errors in the last three places. This verification was performed on the type-written sheets ready for the printer.

This table was then used in computing $\int_x^\infty \frac{e^{-x}}{x}\,dx$ and $\int_x^\infty \frac{e^{-x}}{x^2}\,dx$.

Values of $\frac{e^{-x}-1}{x}$ *from* $x = 0$ *to* $x = 0.100$ *at intervals of* .001 (*Table III*). By division, from Newman's values of e^{-x}; checked by taking the first and second differences on the type-written sheets.

These numbers were used in computing

$$\int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x, \text{ and } \int_x^\infty \frac{e^{-x}}{x^2}\,dx - \frac{1}{x} - \log_e x$$

Values of $\int_x^\infty \frac{e^{-x}}{x}\,dx$ *from* $x = 0.100$ *to* $x = 1.000$ *at intervals of* .001 (*Table I*), *and from* $x = 1.00$ *to* $x = 2.00$ *at intervals of* .01 (*Table II*). It was found impossible to obtain these from Glaisher's table by interpolation. The table was consequently built up from the values of e^{-x}/x by means of the relation

$$\Delta\,.\,Ei\,(-x) = 0.001\,(1 + \tfrac{1}{2}\Delta - \tfrac{1}{12}\Delta^2 + \tfrac{1}{24}\Delta^3 - \tfrac{19}{720}\Delta^4)e^{-x}/x$$

which may be deduced by Taylor's theorem, treating intervals of 0.001 as units.[1]

The computation was carried out with ten places of decimals, and every tenth value was checked by Glaisher's results, and found to agree within a few units in the last place; the tenth place was then rejected. Incidentally the agreement furnishes evidence of the accuracy of Glaisher's Table, at least as far as the ninth decimal place, and of our Table of e^{-x}/x as far as the seventh.

Following Glaisher,[2] the integration constant

$$\gamma = 0.577\ 215\ 665$$

was adopted, whence $Ei(-\infty) = 0$.

Values of $\int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x$ *from* $x = 0$ *to* $x = 0.100$ *at intervals of* .001 (*Table I*). As for $x = 0$, $\int_x^\infty \frac{e^{-x}}{x}\,dx$ becomes infinite, interpolation for low values of x would be impossible. By adding $\log_e x$ however, the infinity is removed and this difficulty is avoided, $\int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x$ for $x = 0$ having the value $-\gamma$. By subtracting the logarithm, $\int_x^\infty \frac{e^{-x}}{x}\,dx$ may be obtained.

The values in the Table were computed in the same manner as those of $\int_x^\infty \frac{e^{-x}}{x}\,dx$, using $\frac{e^{-x}-1}{x}$ in place of $\frac{e^{-x}}{x}$, and every tenth was checked against Glaisher's value for $\int_\infty^x \frac{e^{-x}}{x}\,dx$. The numbers so obtained are *negative*.

For example :

for $x = 0{\cdot}050$, $\int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x = -0.527\ 833\ 785$

hence

$$\begin{aligned}\int_x^\infty \frac{e^{-x}}{x}\,dx &= -0.527\ 833\ 785 - \log_e 0.050\\ &= -0.527\ 833\ 785 + 2.995\ 732\ 274\\ &= \quad 2.467\ 898\ 489\end{aligned}$$

Values of $\int_x^\infty \frac{e^{-x}}{x^2}\,dx$ *from* $x = 0.100$ *to* $x = 1.000$ *at intervals of* .001

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[1] The coefficients are those of the powers of x in the expansion of $\frac{x}{\log_e(1+x)}$. See: Boole, Finite Differences.

[2] In Glaisher's Table the limits are the inverse of ours, hence the minus sign prefixed to his numbers.

(*Table I*), *and from* $x = 1.00$ *to* $x = 2.00$ *at intervals of* .01 (*Table II*). Obtained by subtraction

$$\int_x^\infty \frac{e^{-x}}{x^2}\,dx = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-x}}{x}\,dx$$

and checked by addition.

Values of $\int_x^\infty \frac{e^{-x}}{x^2}\,dx - \frac{1}{x} - \log_e x$ *from* $x = 0$ *to* $x = 0.100$ *at intervals of* .001 (*Table I*). These numbers supplement the values of $\int_x^\infty \frac{e^{-x}}{x^2}\,dx$ in the same way that $\int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x$ supplements those of $\int_x^\infty \frac{e^{-x}}{x}\,dx$. They were obtained by subtraction,

$$\int_x^\infty \frac{e^{-x}}{x^2}\,dx - \frac{1}{x} - \log_e x = \frac{e^{-x}-1}{x} - \left(\int_x^\infty \frac{e^{-x}}{x}dx + \log_e x\right)$$

and checked by addition. As in the case of $\int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x$ the numbers tabulated are negative in sign. For example: for $x = 0.001$

$$\int_x^\infty \frac{e^{-x}}{x^2}\,dx - \frac{1}{x} - \log_e x = -\,0.423\ 283\ 252$$

hence

$$\int_x^\infty \frac{e^{-x}}{x^2}\,dx = -\,0.423\ 283\ 252 + 1000 - 6.907\ 755\ 279$$
$$= 992.668\ 961\ 469$$

Values of $\int_x^\infty xe^{-x}\,dx$ *from* $x = 0$ *to* $x = 1.000$ *at intervals of* .001 (*Table I*), *and from* $x = 1.00$ *to* $x = 2.00$ *at intervals of* .01 (*Table II*). Prepared from Newman's values of e^{-x} by multiplication, according to the formula

$$\int_x^\infty xe^{-x}dx = (1 + x)\,e^{-x}$$

and checked by taking first and second differences from $x = 0$ to $x = 1$, and first, second, and third differences from $x = 1$ to $x = 2$, on the typewritten sheets.

Values of $\int_x^\infty x^2e^{-x}\,dx$ *from* $x=0$ *to* $x = 1.000$ *at intervals of* .001 (*Table I*), *and from* $x = 1.00$ *to* $x = 2.00$ *at intervals of* .01 (*Table II*) From Newman's Table of e^{-x} by multiplication,

$$\int_x^\infty x^2e^{-x}\,dx = \left\{1 + (1 + x)^2\right\}e^{-x}$$

checked by first and second differences between $x = 0$ and $x = 1.000$ and by first, second, and third differences from $x = 1.00$ to $x = 2.00$ on the type-written sheets.

Our thanks are due to Mr. R. F. Stupart, Superintendent of the Meteorological Service, for the use of a 8–16 place arithmometer, which together with a 6–12 place arithmometer and a 9 place comptometer from the School of Practical Science, were of great assistance in computing the tables.

TABLES.

TABLE I. $x = 0$ to $x = 0.100$ at intervals of .001, numerical values of

$$\int_x^\infty \frac{e^{-x}}{x^2}\,dx - \frac{1}{x} - \log_e x, \int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x, \int_x^\infty e^{-x}\,dx, \int_x^\infty xe^{-x}\,dx, \text{ and } \int_x^\infty x^2e^{-x}\,dx.$$

$x = 0.100$ to $x = 1.000$ at intervals of .001, numerical values of

$$\int_x^\infty \frac{e^{-x}}{x^2}dx, \int_x^\infty \frac{e^{-x}}{x}\,dx, \int_x^\infty e^{-x}\,dx. \int_x^\infty xe^{-x}\,dx, \text{ and } \int_x^\infty x^2e^{-x}\,dx.$$

TABLE II. $x = 1.00$ to $x = 2.00$ at intervals of .01, numerical values of

$$\int_x^\infty \frac{e^{-x}}{x^2}\,dx, \int_x^\infty \frac{e^{-x}}{x}\,dx, \int_x^\infty e^{-x}\,dx, \int_x^\infty xe^{-x}\,dx, \text{ and } \int_x^\infty x^2e^{-x}\,dx.$$

TABLE III. $x = 0$ to $x = 0.100$ at intervals of .001, numerical values of $\frac{e^{-x} - 1}{x}$.

$x = 0.100$ to $x = 1.000$ at intervals of .001, numerical values of $\frac{e^{-x}}{x}$.

TABLE IV. $x = 1.00$ to $x = 2.00$ at intervals of .01, numerical values of $\frac{e^{-x}}{x}$.

TABLE 1.

x	$-A$	$-B$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.000	0.422 784 335	0.577 215 665	1.000 000 000	1.000 000 000	2.000 000 000
.001	.423 283 252	.576 216 915	.999 000 500	.999 999 500	.000 000 000
.002	.423 784 002	.575 216 665	.998 001 999	.999 998 003	1.999 999 997
.003	.424 283 585	.574 217 914	.997 004 496	.999 995 509	.999 999 991
.004	.424 783 002	.573 219 662	.996 007 989	.999 992 021	.999 999 979
.005	.425 282 253	.572 221 908	.995 012 479	.999 987 542	.999 999 958
.006	.425 781 338	.571 224 653	.994 017 964	.999 982 071	.999 999 928
.007	.426 280 257	.570 227 896	.993 024 443	.999 975 613	.999 999 886
.008	.426 779 008	.569 231 637	.992 031 915	.999 968 170	.999 999 830
.009	.427 277 595	.568 235 875	.991 040 379	.999 959 742	.999 999 759
.010	.427 776 015	.567 240 610	.990 049 834	.999 950 332	.999 999 669
.011	.428 274 269	.566 245 842	.989 060 279	.999 939 942	.999 999 560
.012	.428 772 358	.565 251 570	.988 071 713	.999 928 573	.999 999 429
.013	.429 270 282	.564 257 794	.987 084 135	.999 916 229	.999 999 275
.014	.429 768 040	.563 264 513	.986 097 544	.999 902 910	.999 999 095
.015	.430 265 632	.562 271 728	.985 111 940	.999 888 619	.999 998 888
.016	.430 763 059	.561 279 438	.984 127 320	.999 873 357	.999 998 651
.017	.431 260 320	.560 287 643	.983 143 685	.999 857 127	.999 998 383
.018	.431 757 416	.559 296 342	.982 161 032	.999 839 931	.999 998 082
.019	.432 254 347	558 305 535	.981 179 362	.999 821 770	.999 997 746
.020	.432 751 113	.557 315 222	.980 198 673	.999 802 647	.999 997 373
.021	.433 247 713	.556 325 403	.979 218 965	.999 782 563	.999 996 961
.022	.433 744 149	.555 336 076	.978 240 235	.999 761 520	.999 996 509
.023	.434 240 420	.554 347 242	.977 262 484	.999 739 521	.999 996 014
.024	.434 736 526	553 358 901	976 285 710	.999 716 567	.999 995 474
.025	.435 232 468	.552 371 051	.975 309 912	.999 692 660	.999 994 888
.026	.455 728 245	.551 383 693	.974 335 090	.999 667 802	.999 994 254
.027	.436 223 857	.550 396 827	.973 361 242	.999 641 994	.999 993 570
.028	.436 719 305	.549 410 452	.972 388 367	.999 615 241	.999 992 835
.029	.437 214 589	.548 424 567	.971 416 464	.999 587 541	.999 992 045
.030	.437 709 709	.547 439 173	.970 445 534	.999 558 900	.999 991 200
.031	.438 204 663	.546 454 270	.969 475 573	.999 529 316	.999 990 299
.032	.438 699 455	.545 469 855	.968 506 582	.999 498 793	.999 989 338
.033	.439 194 081	.544 485 931	.967 538 560	.999 467 332	.999 988 314
.034	.439 688 545	.543 502 495	.966 571 505	.999 434 936	.999 987 228
.035	.440 182 844	.542 519 549	.965 605 416	.999 401 606	.999 986 078
.036	.440 676 980	.541 537 090	.964 640 293	.999 367 344	.999 984 862
.037	.441 170 952	.540 555 120	.963 676 135	.999 332 152	.999 983 577
.038	.441 664 760	.539 573 638	.962 712 941	.999 296 032	.999 982 223
.039	.442 158 405	.538 592 643	.961 750 709	.999 258 987	.999 980 796
.040	.442 651 885	.537 612 136	.960 789 439	.999 221 017	.999 979 297
.041	.443 145 203	.536 632 115	.959 829 130	.999 182 124	.999 977 721
.042	.443 638 358	.535 652 581	.958 869 781	.999 142 311	.999 976 069
.043	.444 131 349	.534 673 533	.957 911 390	.999 101 580	.999 974 338
.044	.444 624 177	.533 694 971	.956 953 957	.999 059 932	.999 972 526
.045	.445 116 842	.532 716 895	.955 997 482	.999 017 368	.999 970 632
.046	.445 609 344	.531 739 304	.955 041 962	.998 973 892	.999 968 654
.047	.446 101 684	.530 762 197	.954 087 398	.998 929 505	.999 966 590
.048	.446 593 860	.529 785 576	.953 133 787	.998 884 209	.999 964 438
.049	.447 085 872	.528 809 438	.952 181 130	.998 838 005	.999 962 197
.050	.447 577 725	.527 833 765	.951 229 425	.998 790 896	.999 959 865

$$A = \int \frac{e^{-x}}{x^2}\,dx - \frac{1}{x} - \log_e x; \quad B = \int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x$$

TABLE 1.

x	$-A$	$-B$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.050	0.447 577 725	0.527 833 785	0.951 229 425	0.998 790 896	1.999 959 865
.051	.448 069 413	.526 858 616	.950 278 671	.998 742 883	.999 957 440
.052	.448 560 929	.525 883 939	.949 328 867	.998 693 968	.999 954 921
.053	.449 052 303	.524 909 726	.948 380 012	.998 644 153	.999 952 306
.054	.449 543 504	.523 936 005	.947 432 107	.998 593 440	.999 949 593
.055	.450 034 544	.522 962 766	.946 485 148	.998 541 831	.999 946 780
.056	.450 525 421	.521 990 010	.945 539 136	.998 489 328	.999 943 866
.057	.451 016 136	.521 017 735	.944 594 069	.998 435 930	.999 940 849
.058	.451 506 688	.520 045 942	.943 649 947	.998 381 644	.999 937 727
.059	.451 997 079	.519 074 630	.942 706 769	.998 326 469	.999 934 499
.060	.452 487 308	.518 103 799	.941 764 534	.998 270 406	.999 931 164
.061	.452 977 375	.517 133 448	.940 823 240	.998 213 457	.999 927 718
.062	.453 467 281	.516 163 577	.939 882 887	.998 155 626	.999 924 161
.063	.453 957 025	.515 194 186	.938 943 474	.998 096 912	.999 920 492
.064	.454 446 608	.514 225 274	.938 005 000	.998 037 319	.999 916 707
.065	.454 936 029	.513 256 842	.937 067 463	.997 976 848	.999 912 807
.066	.455 425 288	.512 288 889	.936 130 864	.997 915 501	.999 908 789
.067	.455 914 387	.511 321 414	.935 195 201	.997 853 280	.999 904 651
.068	.456 403 325	.510 354 417	.934 260 474	.997 790 186	.999 900 392
.069	.456 892 101	.509 387 898	.933 326 680	.997 726 220	.999 896 010
.070	.457 380 716	.508 421 856	.932 393 820	.997 661 387	.999 891 504
.071	.457 869 170	.507 456 293	.931 461 892	.997 595 686	.999 886 872
.072	.458 357 463	.506 491 206	.930 530 896	.997 529 120	.999 882 113
.073	.458 845 596	.505 526 595	.929 600 830	.997 461 691	.999 877 224
.074	.459 333 568	.504 562 461	.928 671 694	997 393 398	.999 872 205
.075	.459 821 379	.503 598 803	.927 743 486	.997 324 248	.999 867 053
.076	.460 309 030	.502 635 621	.926 816 207	.997 254 238	.999 861 767
.077	.460 796 520	.501 672 914	.925 889 854	.997 183 372	.999 856 346
.078	.461 283 849	.500 710 682	.924 964 427	.997 111 652	.999 850 787
.079	.461 771 019	.499 748 925	.924 039 924	.997 039 078	.999 845 090
.080	.462 258 028	.498 787 642	.923 116 346	.996 965 654	.999 839 253
.081	.462 744 878	.497 826 833	.922 193 691	.996 891 380	.999 833 274
.082	.463 231 567	.496 866 498	.921 271 959	.996 816 259	.999 827 151
.083	.463 718 095	.495 906 637	.920 351 147	.996 740 292	.999 820 884
.084	.464 204 464	.494 947 249	.919 431 256	.996 663 482	.999 814 470
.085	.464 690 674	.493 988 333	.918 512 284	.996 585 828	.999 807 908
.086	.465 176 723	.493 029 891	.917 594 231	.996 507 335	.999 801 197
.087	.465 662 613	.492 071 920	.916 677 096	.996 428 003	.999 794 335
.088	.466 148 344	.491 114 421	.915 760 877	.996 347 834	.999 787 320
.089	.466 633 914	.490 157 394	.914 845 574	.996 266 829	.999 780 151
.090	.467 119 325	.489 200 839	.913 931 185	.996 184 992	.999 772 826
.091	.467 604 577	.488 244 754	.913 017 711	.996 102 323	.999 765 345
.092	.468 089 669	.487 289 140	.912 105 150	.996 018 823	.999 757 705
.093	.468 574 603	.486 333 996	.911 193 500	.995 934 496	.999 749 904
.094	.469 059 377	.485 379 323	.910 282 762	.995 849 342	.999 741 942
.095	.469 543 992	.484 425 119	.909 372 934	.995 763 363	.999 733 817
.096	.470 028 449	.483 471 384	.908 464 016	.995 676 562	.999 725 528
.097	.470 512 746	.482 518 119	.907 556 006	.995 588 939	.999 717 072
.098	.470 996 884	.481 565 323	.906 648 904	.995 500 496	.999 708 449
.099	.471 480 864	.480 612 994	.905 742 708	.995 411 236	.999 699 657
.100	.471 964 685	.479 661 135	.904 837 418	.995 321 160	.999 690 694

$$A = \int_x^\infty \frac{e^{-x}}{x^2}\,dx - \frac{1}{x} - \log_e x\,; \quad B = \int_x^\infty \frac{e^{-x}}{x}\,dx + \log_e x$$

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}dx$	$\int_x^\infty xe^{-x}dx$	$\int_x^\infty x^2e^{-x}dx$
.100	7.225 450 222	1.822 923 958	0.904 837 418	0.995 321 160	1.999 690 694
.101	.135 906 990	.813 925 019	.903 933 033	.995 230 269	.999 681 559
.102	.048 207 252	.805 023 647	.903 029 552	.995 138 566	.999 672 251
.103	6.962 296 377	.796 217 930	.902 126 973	.995 046 052	.999 662 769
.104	.878 121 851	.787 506 009	.901 225 297	.994 952 728	.999 653 110
.105	.795 633 182	.778 886 081	.900 324 523	.994 858 597	.999 643 273
.106	.714 781 795	.770 356 394	.899 424 648	.994 763 661	.999 633 257
.107	.635 520 951	.761 915 245	.898 525 673	.994 667 919	.999 623 060
.108	.557 805 656	.753 560 978	.897 627 596	.994 571 376	.999 612 682
.109	.481 592 581	.745 291 983	.896 730 417	.994 474 033	.999 602 120
.110	.406 839 991	.737 106 694	.895 834 135	.994 375 890	.999 591 373
.111	.333 507 663	.729 003 589	.894 938 749	.994 276 950	.999 580 440
.112	.261 556 829	.720 981 184	.894 044 257	.994 177 214	.999 569 320
.113	.190 950 104	.713 038 038	.893 150 660	.994 076 685	.999 558 010
.114	.121 651 428	.705 172 746	.892 257 956	.993 975 362	.999 546 510
.115	.053 626 007	.697 383 940	.891 366 144	.993 873 250	.999 534 818
.116	5.986 840 258	.689 670 288	.890 475 223	.993 770 349	.999 522 933
.117	.921 261 757	.682 030 492	.889 585 193	.993 666 660	.999 510 853
118	.856 859 193	.674 463 287	.888 696 053	.993 562 187	.999 498 577
.119	.793 602 313	.666 967 441	.887 807 801	.993 456 929	.999 486 103
.120	.731 461 887	.659 541 752	.886 920 437	.993 350 889	.999 473 433
.121	.670 409 659	.652 185 048	.886 033 960	.993 244 069	.999 460 561
.122	.610 418 310	.644 896 186	.885 148 369	.993 136 469	.999 447 487
.123	.551 461 416	.637 674 052	.884 263 663	.993 028 093	.999 434 211
.124	.493 513 418	.630 517 557	.883 379 841	.992 918 941	.999 420 731
.125	.436 549 580	.623 425 641	.882 496 903	.992 809 015	.999 407 045
126	.380 545 962	.616 397 266	.881 614 847	.992 698 317	.999 393 152
.127	.325 479 387	.609 431 421	.880 733 673	.992 586 849	.999 379 051
.128	.271 327 406	.602 527 119	.879 853 379	.992 474 612	.999 364 741
.129	.218 068 277	.595 683 394	.878 973 966	.992 361 606	.999 350 220
.130	.165 680 933	.588 899 305	.878 095 431	.992 247 837	.999 335 487
.131	.114 144 958	.582 173 930	.877 217 774	.992 133 303	.999 320 540
.132	.063 440 561	.575 506 371	.876 340 995	.992 018 006	.999 305 378
.133	.013 548 555	.568 895 747	.875 465 092	.991 901 949	.999 290 001
.134	4.964 450 328	.562 341 199	.874 590 065	.991 785 133	.999 274 406
.135	.916 127 829	.555 841 887	.873 715 912	.991 667 560	.999 258 592
.136	.868 563 544	.549 396 989	.872 842 632	.991 549 231	.999 242 558
.137	.821 740 475	.543 005 701	.871 970 226	.991 430 147	.999 226 303
.138	.775 642 123	.536 667 237	.871 098 692	.991 310 311	.999 209 826
.139	.730 252 470	.530 380 828	.870 228 028	.991 189 724	.999 193 125
.140	.685 555 959	.524 145 722	.869 358 235	.991 068 388	.999 176 198
.141	.641 537 483	.517 961 182	.868 489 312	.990 946 305	.999 159 044
.142	.598 182 362	.511 826 487	.867 621 256	.990 823 475	.999 141 665
.143	.555 476 333	.505 740 932	.866 754 069	.990 699 901	.999 124 055
.144	.513 405 537	.499 703 825	.865 887 748	.990 575 584	.999 106 216
.145	.471 956 497	.493 714 490	.865 022 293	.990 450 525	.999 088 145
.146	.431 116 114	.487 772 264	.864 157 703	.990 324 728	.999 069 841
.147	.390 871 647	.481 876 499	.863 293 977	.990 198 192	.999 051 304
.148	.351 210 705	.476 026 558	.862 431 115	.990 070 920	.999 032 531
.149	.312 121 234	.470 221 819	.861 569 115	.989 942 913	.999 013 522
.150	.273 591 506	.464 461 670	.860 707 976	.989 814 173	.998 994 275

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}dx$
.150	4.273 591 506	1.464 461 670	0.860 707 976	0.989 814 173	1.998 994 275
.151	.235 610 105	.458 745 515	.859 847 699	.989 684 701	.998 974 790
.152	.198 165 923	.453 072 766	.858 988 281	.989 554 499	.998 955 064
.153	.161 248 144	.447 442 848	.858 129 722	.989 423 569	.998 935 097
.154	.124 846 237	.441 855 198	.857 272 021	.989 291 913	.998 914 888
.155	.088 949 948	.436 309 262	.856 415 177	.989 159 529	.998 894 435
.156	.053 549 284	.430 804 500	.855 559 190	.989 026 424	.998 873 737
.157	.018 634 518	.425 340 379	.854 704 059	.988 892 596	.998 852 792
.158	3.984 196 166	.419 916 378	.853 849 782	.988 758 048	.998 831 601
.159	.950 224 990	.414 531 985	.852 996 359	.988 622 780	.998 810 161
.160	.916 711 982	.409 186 699	.852 143 789	.988 486 795	.998 788 471
.161	.883 648 367	.403 880 025	.851 292 071	.988 350 095	.998 766 531
.162	.851 025 583	.398 611 482	.850 441 205	.988 212 680	.998 744 338
.163	.818 835 286	393 380 594	.849 591 188	.988 074 552	.998 721 893
.164	.787 069 335	.388 186 896	.848 742 022	.987 935 713	.998 699 192
.165	.755 719 791	.383 029 931	.847 893 704	.987 796 165	.998 676 237
.166	.724 778 909	.377 909 249	.847 046 234	.987 655 909	.998 653 024
.167	.694 239 132	.372 824 409	.846 199 611	.987 514 946	.998 629 554
.168	.664 093 085	.367 774 979	.845 353 835	.987 373 279	.998 605 824
.169	.634 333 571	.362 760 532	.844 508 903	.987 230 908	.998 581 835
.170	.604 953 563	.357 780 652	.843 664 817	.987 087 835	.998 557 584
.171	.575 946 203	.352 834 928	.842 821 573	.986 944 063	.998 533 071
.172	.547 304 794	.347 922 957	.841 979 173	.986 799 591	.998 508 294
.173	.519 022 796	.343 041 342	.841 137 615	.986 654 422	.998 483 252
.174	.491 093 821	.338 193 694	.840 296 898	.986 508 558	.998 457 945
.175	463 511 632	.333 385 630	.839 457 021	.986 361 999	.998 432 370
.176	.436 270 130	.328 604 775	.838 617 983	.986 214 748	.998 406 527
.177	.409 363 363	.323 855 759	.837 779 785	.986 066 806	.998 380 416
.178	.382 785 510	.319 138 217	.836 942 423	.985 918 175	.998 354 033
.179	.356 530 885	.314 451 793	.836 105 899	.985 768 854	.998 327 380
.180	.330 593 928	.309 796 135	.835 270 211	.985 618 849	.998 300 454
.181	.304 969 205	.305 170 898	.834 435 359	.985 468 159	.998 273 254
.182	.279 651 403	.300 575 742	.833 601 340	.985 316 784	.998 245 780
.183	.254 635 327	.296 010 333	.832 768 156	.985 164 728	.998 218 029
.184	.229 915 895	.291 474 343	.831 935 804	.985 011 992	.998 190 002
.185	.205 488 142	.286 967 446	.831 104 284	.984 858 576	.998 161 697
.186	.181 347 206	.282 489 326	.830 273 595	.984 704 483	.998 133 113
.187	.157 488 332	.278 039 670	.829 443 736	.984 549 715	.998 104 248
.188	.133 906 870	.273 618 168	.828 614 707	.984 394 272	.998 075 103
.189	.110 598 268	.269 224 519	.827 786 507	.984 238 156	998 045 675
.190	.087 558 070	.264 858 424	.826 959 134	.984 081 369	.998 015 964
.191	.064 781 919	.260 519 590	.826 132 588	.983 923 913	.997 985 968
.192	.042 265 547	.256 207 726	.825 306 868	.983 765 787	.997 955 687
.193	.020 004 778	.251 922 549	.824 481 974	.983 606 995	.997 925 119
.194	2.997 995 521	.247 663 779	.823 657 904	.983 447 538	.997 894 264
.195	.976 233 774	.243 431 139	.822 834 658	.983 287 416	.997 863 121
.196	.954 715 614	.239 224 359	.822 012 235	.983 126 633	.997 831 687
.197	.933 437 201	.235 043 171	.821 190 633	.982 965 188	.997 799 963
.198	.912 394 776	.230 887 311	.820 369 853	.982 803 082	.997 767 948
.199	.891 584 652	.226 756 521	.819 549 893	.982 640 322	.997 735 640
.200	.871 003 221	.222 650 544	818 730 753	.982 476 904	.997 703 038

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.200	2.871 003 221	1.222 650 544	0.818 730 753	0.982 476 904	1.997 703 038
.201	.850 646 947	.218 569 130	.817 912 432	.982 312 830	.997 670 141
.202	.830 512 366	.214 512 030	.817 094 928	.982 148 103	.997 636 948
.203	.810 596 081	.210 479 000	.816 278 241	.981 982 724	.997 603 459
.204	.790 894 765	.206 469 800	.815 462 371	.981 816 695	.997 569 672
.205	.771 405 155	.202 484 193	.814 647 316	.981 650 016	.997 535 586
.206	.752 124 057	.198 521 944	.813 833 076	.981 482 690	.997 501 200
.207	.733 048 335	.194 582 824	.813 019 650	.981 314 718	.997 466 514
.208	.714 174 916	.190 666 607	.812 207 037	.981 146 100	.997 431 526
.209	.695 500 787	.186 773 068	.811 395 236	.980 976 840	.997 396 235
.210	.677 022 995	.182 901 986	.810 584 246	.980 806 938	.997 360 640
.211	.658 738 640	.179 053 146	.809 774 067	.980 636 394	.997 324 741
.212	.640 644 883	.175 226 332	.808 964 698	.980 465 213	.997 288 536
.213	.622 738 936	.171 421 333	.808 156 137	.980 293 394	.997 252 025
.214	.605 018 063	.167 637 942	.807 348 385	.980 120 939	.997 215 205
.215	.587 479 583	.163 875 953	.806 541 440	.979 947 850	.997 178 078
.216	.570 120 863	.160 135 164	.805 735 302	.979 774 127	.997 140 640
.217	.552 939 322	.156 415 375	.804 929 969	.979 599 773	.997 102 893
.218	.535 932 425	.152 716 390	.804 125 442	.979 424 788	.997 064 833
.219	.519 097 686	.149 038 013	.803 321 718	.979 249 174	.997 026 462
.220	.502 432 663	.145 380 055	.802 518 798	.979 072 934	.996 987 777
.221	.485 934 960	.141 742 326	.801 716 680	.978 896 067	.996 948 778
.222	.469 602 227	.138 124 639	.800 915 364	.978 718 575	.996 909 463
.223	.453 432 154	.134 526 811	.800 114 849	.978 540 461	.996 869 833
.224	.437 422 475	.130 948 661	.799 315 134	.978 361 725	.996 829 885
.225	.421 570 962	.127 390 010	.798 516 219	.978 182 368	.996 789 620
.226	.405 875 434	.123 850 680	.797 718 102	.978 002 393	.996 749 035
.227	.390 333 739	.120 330 500	.796 920 782	.977 821 800	.996 708 131
.228	.374 943 774	.116 829 295	.796 124 260	.977 640 590	.996 666 906
.229	.359 703 468	.113 346 897	.795 328 534	.977 458 768	.996 625 359
.230	.344 610 785	.109 883 139	.794 533 603	.977 276 331	.996 583 490
.231	.329 663 731	.106 437 854	.793 739 466	.977 093 283	.996 541 297
.232	.314 860 340	.103 010 881	.792 946 123	.976 909 624	.996 498 780
.233	.300 198 686	.099 602 059	.792 153 574	.976 725 356	.996 455 938
.234	.285 676 874	.096 211 228	.791 361 816	.976 540 481	.996 412 769
.235	.271 293 044	.092 838 231	.790 570 850	.976 354 999	.996 369 274
.236	.257 045 361	.089 482 914	.789 780 674	.976 168 913	.996 325 450
.237	.242 932 041	.086 145 124	.788 991 288	.975 982 223	.996 281 298
.238	.228 951 304	.082 824 709	.788 202 691	.975 794 932	.996 236 816
.239	.215 101 416	.079 521 522	.787 414 882	.975 607 039	.996 192 004
.240	.201 380 673	.076 235 415	.786 627 861	.975 418 548	.996 146 860
.241	.187 787 394	.072 966 242	.785 841 626	.975 229 458	.996 101 384
.242	.174 319 932	.069 713 860	.785 056 178	975 039 773	.996 055 575
.243	.160 976 658	.066 478 127	.784 271 514	.974 849 492	.996 009 432
.244	.147 755 991	.063 258 904	.783 487 634	.974 658 617	.995 962 954
.245	.134 656 349	.060 056 052	.782 704 538	.974 467 150	.995 916 140
.246	.121 676 196	.056 869 434	.781 922 225	.974 275 092	.995 868 990
.247	.108 814 013	.053 698 916	.781 140 694	.974 082 445	.995 821 502
.248	.096 068 311	.050 544 364	.780 359 943	.973 889 209	.995 773 676
.249	.083 437 620	.047 405 647	.779 579 973	.973 695 387	.995 725 511
.250	070 920 498	.044 282 634	.778 800 783	.973 500 979	.995 677 007

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}dx$
.250	2.070 920 498	1.044 282 634	0.778 800 783	0.973 500 979	1.995 677 007
.251	.058 515 525	.041 175 198	.778 022 372	.973 305 987	.995 628 161
.252	.046 221 305	.038 083 211	.777 244 738	.973 110 412	.995 578 974
.253	.034 036 463	.035 006 548	.776 467 882	.972 914 255	.995 529 444
.254	.021 959 648	.031 945 084	.775 691 802	.972 717 520	.995 479 572
.255	.009 989 530	.028 898 697	.774 916 498	.972 520 205	.995 429 355
.256	1.998 124 799	.025 867 267	.774 141 969	.972 322 313	.995 378 794
.257	.986 364 166	.022 850 674	.773 368 214	.972 123 845	.995 327 887
.258	.974 706 365	.019 848 798	.772 595 232	.971 924 802	.995 276 633
.259	.963 150 148	.016 861 524	.771 823 023	.971 725 186	.995 225 032
.260	.951 694 285	.013 888 737	.771 051 586	.971 524 998	.995 173 083
.261	.940 337 570	.010 930 321	.770 280 920	.971 324 240	.995 120 786
.262	.929 078 812	.007 986 164	.769 511 024	.971 122 912	.995 068 139
.263	.917 916 840	.005 056 154	.768 741 897	.970 921 016	.995 015 141
.264	.906 850 500	.002 140 181	.767 973 540	.970 718 554	.994 961 792
.265	.895 878 656	0.999 238 136	.767 205 950	.970 515 527	.994 908 091
.266	.885 000 191	.996 349 912	.766 439 128	.970 311 935	.994 854 038
.267	.874 214 005	.993 475 401	.765 673 071	.970 107 782	.994 799 631
.268	.863 519 014	.990 614 498	.764 907 781	.969 903 066	.994 744 869
.269	.852 914 149	.987 767 099	.764 143 256	.969 697 791	.994 689 753
.270	842 398 360	.984 933 101	.763 379 494	.969 491 958	.994 634 281
.271	.831 970 610	.982 112 403	.762 616 496	.969 285 567	.994 578 452
.272	.821 629 881	.979 304 902	.761 854 261	.969 078 620	.994 522 266
.273	.811 375 169	.976 510 500	.761 092 788	.968 871 118	.994 465 722
.274	.801 205 483	.973 729 098	.760 332 075	.968 663 064	.994 408 819
.275	.791 119 850	.970 960 598	.759 572 123	.968 454 457	.994 351 556
.276	.781 117 308	.968 204 905	.758 812 931	.968 245 300	.994 293 933
.277	.771 196 912	.965 461 922	.758 054 497	.968 035 593	.994 235 949
.278	.761 357 730	.962 731 556	.757 296 822	.967 825 338	.994 177 603
.279	.751 598 843	.960 013 713	.756 539 903	.967 614 536	.994 118 895
.280	.741 919 348	.957 308 300	.755 783 741	.967 403 189	.994 059 823
.281	.732 318 351	.954 615 227	.755 028 335	.967 191 298	.994 000 388
.282	.722 794 975	.951 934 403	.754 273 685	.966 978 864	.993 940 588
.283	.713 348 352	949 265 739	.753 519 788	.966 765 888	.993 880 422
.284	.703 977 631	.946 609 146	.752 766 645	.966 552 372	.993 819 890
.285	694 681 970	.943 964 536	.752 014 254	.966 338 317	.993 758 991
.286	.685 460 539	.941 331 824	.751 262 616	.966 123 724	.993 697 725
.287	.676 312 526	.938 710 923	.750 511 729	.965 908 595	.993 636 091
.288	.667 237 113	.936 101 749	.749 761 592	.965 692 931	.993 574 087
.289	.658 233 517	.933 504 218	.749 012 205	.965 476 733	.993 511 714
.290	.649 300 953	.930 918 246	.748 263 568	.965 260 002	.993 448 970
.291	.640 438 647	.928 343 752	.747 515 678	.965 042 740	.993 385 856
.292	.631 645 839	.925 780 654	.746 768 536	.964 824 949	.993 322 369
.293	.622 921 779	.923 228 872	.746 022 141	.964 606 628	.993 258 511
.294	.614 265 726	.920 688 327	.745 276 491	.964 387 780	.993 194 279
.295	.605 676 952	.918 158 938	.744 531 587	.964 168 406	.993 129 673
.296	.597 154 736	.915 640 629	.743 787 428	.963 948 507	.993 064 693
.297	.588 698 369	.913 133 322	.743 044 012	.963 728 084	.992 999 337
.298	.580 307 153	.910 636 940	.742 301 340	.963 507 139	.992 933 606
.299	.571 980 396	.908 151 408	.741 559 409	.963 285 673	.992 867 498
.300	.563 717 417	.905 676 652	.740 818 221	.963 063 687	.992 801 014

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}dx$	$\int_x^\infty xe^{-x}dx$	$\int_x^\infty x^2e^{-x}dx$
.300	1.563 717 417	0.905 676 652	0.740 818 221	0.963 063 687	1.992 801 014
.301	.555 517 546	.903 212 596	.740 077 773	.962 841 182	.992 734 151
.302	.547 380 121	.900 759 167	.739 338 065	.962 618 160	.992 666 910
.303	.539 304 487	.898 316 293	.738 599 096	.962 394 623	.992 599 290
.304	.531 290 002	.895 883 901	.737 860 866	.962 170 570	.992 531 290
.305	.523 336 028	.893 461 921	.737 123 374	.961 946 004	.992 462 909
.306	.515 441 938	.891 050 282	.736 386 619	.961 720 925	.992 394 148
.307	.507 607 115	.888 648 914	.735 650 601	.961 495 335	.992 325 004
.308	.499 830 948	.886 257 747	.734 915 318	.961 269 236	.992 255 479
.309	.492 112 833	.883 876 714	.734 180 770	.961 042 628	.992 185 570
.310	.484 452 177	.881 505 746	.733 446 956	.960 815 513	.992 115 278
.311	.476 848 395	.879 144 775	.732 713 876	.960 587 891	.992 044 601
.312	.469 300 905	.876 793 737	.731 981 528	.960 359 765	.991 973 540
.313	.461 809 137	.874 452 564	.731 249 913	.960 131 135	.991 902 093
.314	.454 372 528	.872 121 192	.730 519 028	.959 902 003	.991 830 260
.315	.446 990 521	.869 799 556	.729 788 874	.959 672 370	.991 758 040
.316	.439 662 568	.867 487 591	.729 059 450	.959 442 235	.991 685 433
.317	.432 388 123	.865 185 234	.728 330 755	.959 211 604	.991 612 438
.318	.425 166 660	.862 892 423	.727 602 788	.958 980 475	.991 539 055
.319	.417 997 643	.860 609 095	.726 875 549	.958 748 850	.991 465 282
.320	.410 880 552	.858 335 189	.726 149 037	.958 516 729	.991 391 119
.321	.403 814 873	.856 070 644	.725 423 251	.958 284 115	.991 316 566
.322	.396 800 100	.853 815 398	.724 698 190	.958 051 008	.991 241 622
.323	.389 835 729	.851 569 393	.723 973 854	.957 817 409	.991 166 287
.324	.382 921 267	.849 332 568	.723 250 242	.957 583 321	.991 090 559
.325	.376 056 222	.847 104 866	.722 527 354	.957 348 744	.991 014 439
.326	.369 240 115	.844 886 227	.721 805 187	.957 113 678	.990 937 925
.327	.362 472 467	.842 676 594	.721 083 743	.956 878 127	.990 861 018
.328	.355 752 809	.840 475 910	.720 363 020	.956 642 090	.990 783 715
.329	.349 080 675	.838 284 118	.719 643 017	.956 405 569	.990 706 018
.330	.342 455 607	.836 101 161	.718 923 733	.956 168 565	.990 627 925
.331	.335 877 151	.833 926 985	.718 205 169	.955 931 080	.990 549 437
.332	.329 344 859	.831 761 535	.717 487 323	.955 693 114	.990 470 551
.333	.322 858 292	.829 604 754	.716 770 194	.955 454 669	.990 391 268
.334	.316 417 005	.827 456 591	.716 053 782	.955 215 745	.990 311 587
.335	.310 020 582	.825 316 989	.715 338 086	.954 976 345	.990 231 507
.336	.303 668 584	.823 185 898	.714 623 106	.954 736 469	.990 151 029
.337	.297 360 594	.821 063 263	.713 908 840	.954 496 119	.990 070 151
.338	.291 096 197	.818 949 033	.713 195 288	.954 255 294	.989 988 873
.339	.284 874 984	.816 843 155	.712 482 449	.954 013 999	989 907 194
.340	.278 696 546	.814 745 580	.711 770 323	.953 772 233	.989 825 114
.341	.272 560 486	.812 656 254	.711 058 908	.953 529 996	.989 742 633
.342	.266 466 404	.810 575 130	.710 348 205	.953 287 291	.989 659 749
.343	.260 413 914	.808 502 155	.709 638 212	.953 044 118	.989 576 462
.344	.254 402 626	.806 437 281	.708 928 928	.952 800 479	.989 492 772
.345	.248 432 159	.804 380 459	.708 220 353	.952 556 375	.989 408 678
.346	.242 502 137	.802 331 640	.707 512 487	.952 311 808	.989 324 180
.347	.236 612 188	.800 290 775	.706 805 328	.952 066 777	.989 239 277
.348	.230 761 941	.798 257 818	.706 098 876	.951 821 255	.989 153 969
.349	.224 951 034	.796 232 720	.705 393 130	.951 575 333	.989 068 254
.350	.219 179 107	.794 215 435	.704 688 090	.951 328 921	.988 982 133

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.350	1.219 179 107	0.794 215 435	0.704 688 090	0.951 328 921	1.988 982 133
.351	.213 445 805	.792 205 915	.703 983 754	.951 082 052	.988 895 605
.352	.207 750 776	.790 204 116	.703 280 122	.950 834 725	.988 808 670
.353	.202 093 674	.788 209 990	.702 577 193	.950 586 943	.988 721 327
.354	.196 474 155	.786 223 493	.701 874 967	.950 338 706	.988 633 575
.355	.190 891 880	.784 244 580	.701 173 443	.950 090 016	.988 545 414
.356	.185 346 514	.782 273 206	.700 472 620	.949 840 873	.988 456 844
.357	.179 837 726	.780 309 326	.699 772 498	.949 591 279	.988 367 864
.358	.174 365 190	.778 352 897	.699 073 075	.949 341 236	.988 278 473
.359	.168 928 580	.776 403 875	.698 374 351	.949 090 744	.988 188 672
.360	.163 527 577	.774 462 218	.697 676 326	.948 839 803	.988 098 459
.361	.158 161 865	.772 527 881	.696 978 998	.948 588 417	.988 007 834
.362	.152 831 131	.770 600 824	.696 282 368	.948 336 585	.987 916 797
.363	.147 535 067	.768 681 003	.695 586 433	.948 084 309	.987 825 346
.364	.142 273 366	.766 768 378	.694 891 195	.947 831 590	.987 733 483
.365	.137 045 727	.764 862 906	.694 196 651	.947 578 428	.987 641 206
.366	.131 851 850	.762 964 547	.693 502 801	.947 324 826	.987 548 514
.367	.126 691 440	.761 073 260	.692 809 645	.947 070 785	.987 455 408
.368	.121 564 207	.759 189 004	.692 117 182	.946 816 305	.987 361 886
.369	.116 469 860	.757 311 740	.691 425 410	.946 561 387	.987 267 949
.370	.111 408 114	.755 441 428	.690 734 331	.946 306 033	.987 173 596
.371	.106 378 688	.753 578 028	.690 043 942	.946 050 244	.987 078 826
.372	.101 381 301	.751 721 501	.689 354 243	.945 794 021	.986 983 639
.373	.096 415 678	.749 871 810	.688 665 233	.945 537 365	.986 888 035
.374	.091 481 545	.748 028 914	.687 976 912	.945 280 277	.986 792 012
.375	.086 578 634	.746 192 776	.687 289 279	.945 022 757	.986 695 572
.376	.081 706 677	.744 363 358	.686 602 333	.944 764 810	.986 598 712
.377	.076 865 408	.742 540 624	.685 916 074	.944 506 434	.986 501 433
.378	.072 054 568	.740 724 534	.685 230 501	.944 247 630	.986 403 735
.379	.067 273 899	.738 915 053	.684 545 613	.943 988 400	.986 305 616
.380	.062 523 143	.737 112 144	.683 861 409	.943 728 745	.986 207 077
.381	.057 802 050	.735 315 771	.683 177 890	.943 468 666	.986 108 117
.382	.053 110 368	.733 525 897	.682 495 053	.943 208 164	.986 008 735
.383	.048 447 852	.731 742 486	.681 812 899	.942 947 240	.985 908 932
.384	.043 814 254	.729 965 504	.681 131 427	.942 685 895	.985 808 706
.385	.039 209 335	.728 194 915	.680 450 636	.942 424 131	.985 708 058
.386	.034 632 854	.726 430 684	.679 770 526	.942 161 949	.985 606 986
.387	.030 084 575	.724 672 776	.679 091 095	.941 899 349	.985 505 492
.388	.025 564 263	.722 921 158	.678 412 343	.941 636 332	.985 403 573
.389	.021 071 687	.721 175 794	.677 734 270	.941 372 901	.985 301 230
.390	.016 606 616	.719 436 652	.677 056 874	.941 109 056	.985 198 462
.391	.012 168 826	.717 703 696	.676 380 156	.940 844 797	.985 095 269
.392	.007 758 090	.715 976 895	.675 704 114	.940 580 127	.984 991 650
.393	.003 374 186	.714 256 215	.675 028 748	.940 315 045	.984 887 606
.394	0.999 016 893	.712 541 625	.674 354 056	.940 049 554	.984 783 135
.395	.994 685 999	.710 833 088	.673 680 039	.939 783 655	.984 678 238
.396	.990 381 283	.709 130 575	.673 006 696	.939 517 347	.984 572 913
.397	.986 102 535	.707 434 053	.672 334 026	.939 250 634	.984 467 161
.398	.981 849 543	.705 743 491	.671 662 028	.938 983 515	.984 360 981
.399	.977 622 099	.704 058 857	.670 990 701	.938 715 991	.984 254 373
400	.973 419 996	.702 380 119	.670 320 046	.938 448 064	.984 147 336

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}\,dx$	$\int_x^\infty \frac{e^{-x}}{x}\,dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.400	0.973 419 996	0.702 380 119	0.670 320 046	0.938 448 064	1.984 147 336
.401	.969 243 031	.700 707 246	.669 650 061	.938 179 735	.984 039 870
.402	.965 091 000	.699 040 208	.668 980 746	.937 911 005	.983 931 975
.403	.960 963 705	.697 378 973	.668 312 099	.937 641 875	.983 823 650
.404	.956 860 947	.695 723 512	.667 644 121	.937 372 346	.983 714 895
.405	.952 782 529	.694 073 794	.666 976 811	.937 102 419	.983 605 710
.406	.948 728 258	.692 429 790	.666 310 167	.936 832 095	.983 496 094
.407	.944 697 942	.690 791 469	.665 644 190	.936 561 376	.983 386 046
.408	.940 691 392	.689 158 801	.664 978 879	.936 290 261	.983 275 567
.409	.936 708 418	.687 531 759	.664 314 232	.936 018 753	.983 164 656
.410	.932 748 836	.685 910 311	.663 650 250	.935 746 853	.983 053 312
.411	.928 812 459	.684 294 431	.662 986 932	.935 474 560	.982 941 535
.412	.924 899 106	.682 684 088	.662 324 276	.935 201 878	.982 829 327
.413	.921 008 597	.681 079 255	.661 662 283	.934 928 806	.982 716 685
.414	.917 140 752	.679 479 903	.661 000 951	.934 655 345	.982 603 609
.415	.913 295 395	.677 886 004	.660 340 281	.934 381 497	.982 490 099
.416	.909 472 350	.676 297 531	.659 680 270	.934 107 263	.982 376 155
.417	.905 671 444	.674 714 455	.659 020 920	.933 832 643	.982 261 776
.418	.901 892 505	.673 136 750	.658 362 228	.933 557 640	.982 146 962
.419	.898 135 362	.671 564 388	.657 704 195	.933 282 253	.982 031 712
.420	.894 399 849	.669 997 341	.657 046 820	.933 006 484	.981 916 027
.421	.890 685 797	.668 435 584	.656 390 101	.932 730 334	.981 799 906
.422	.886 993 041	.666 879 090	.655 734 039	.932 453 804	.981 683 349
.423	.883 321 420	.665 327 831	.655 078 633	.932 176 895	.981 566 355
.424	.879 670 770	.663 781 782	.654 423 882	.931 899 607	.981 448 923
.425	.876 040 929	.662 240 918	.653 769 785	.931 621 944	.981 331 055
.426	.872 431 743	.660 705 210	.653 116 342	.931 343 904	.981 212 749
.427	.868 843 052	.659 174 635	.652 463 552	.931 065 489	.981 094 005
.428	.865 274 700	.657 649 166	.651 811 415	.930 786 700	.980 974 823
.429	.861 726 534	.656 128 779	.651 159 929	.930 507 539	.980 855 202
.430	.858 198 401	.654 613 447	.650 509 095	.930 228 005	.980 735 143
.431	.854 690 149	.653 103 147	.649 858 911	.929 948 101	.980 614 644
.432	.851 201 630	.651 597 853	.649 209 377	.929 667 827	.980 493 706
.433	.847 732 695	.650 097 540	.648 560 492	.929 387 185	.980 372 328
.434	.844 283 197	.648 602 184	.647 912 255	.929 106 174	.980 250 510
.435	.840 852 991	.647 111 761	.647 264 667	.928 824 797	.980 128 251
.436	.837 441 933	.645 626 246	.646 617 726	.928 543 054	.980 005 552
.437	.834 049 878	.644 145 617	.645 971 431	.928 260 947	.979 882 412
.438	.830 676 688	.642 669 848	.645 325 783	.927 978 476	.979 758 831
.439	.827 322 222	.641 198 916	.644 680 780	.927 695 642	.979 634 808
.440	.823 986 341	.639 732 798	.644 036 421	.927 412 446	.979 510 344
.441	.820 668 908	.638 271 470	.643 392 707	.927 128 890	.979 385 437
.442	.817 369 787	.636 814 909	.642 749 635	.926 844 974	.979 260 088
.443	.814 088 842	.635 363 093	.642 107 207	.926 560 700	.979 134 297
.444	.810 825 941	.633 915 998	.641 465 421	.926 276 068	.979 008 063
.445	.807 580 952	.632 473 601	.640 824 276	.925 991 079	.978 881 385
.446	.804 353 742	.631 035 881	.640 183 772	.925 705 734	.978 754 264
.447	.801 144 184	.629 602 814	.639 543 908	.925 420 035	.978 626 699
.448	.797 952 147	.628 174 380	.638 904 684	.925 133 981	.978 498 691
.449	.794 777 505	.626 750 554	.638 266 099	.924 847 577	.978 370 238
.450	.791 620 132	.625 331 316	.637 628 152	.924 560 820	.978 241 340

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}dx$
.450	0.791 620 132	0.625 331 316	0.637 628 152	0.924 560 820	1.978 241 340
.451	.788 479 902	.623 916 644	.636 900 842	.924 273 712	.978 111 998
.452	.785 356 691	.622 506 516	.636 354 170	.923 986 254	.977 982 211
.453	.782 250 378	.621 100 910	.635 718 134	.923 698 448	.977 851 979
.454	.779 160 840	.619 699 806	.635 082 733	.923 410 294	.977 721 301
.455	.776 087 956	.618 303 182	.634 447 968	.923 121 793	.977 590 177
.456	.773 031 608	.616 911 017	.633 813 837	.922 832 947	.977 458 608
.457	.769 991 677	.615 523 290	.633 180 340	.922 543 756	.977 326 592
.458	.766 968 047	.614 139 980	.632 547 476	.922 254 220	.977 194 129
.459	.763 960 599	.612 761 067	.631 915 245	.921 964 342	.977 061 220
.460	.760 969 221	.611 386 530	.631 283 646	.921 674 122	.976 927 864
.461	.757 993 797	.610 016 349	.630 652 677	.921 383 562	.976 794 061
.462	.755 034 215	.608 650 503	.630 022 340	.921 092 661	.976 659 809
.463	.752 090 363	.607 288 973	.629 392 633	.920 801 421	.976 525 112
.464	.749 162 129	.605 931 738	.628 763 554	.920 509 844	.976 389 966
.465	.746 249 405	.604 578 778	.628 135 105	.920 217 929	.976 254 371
.466	.743 352 080	.603 230 075	.627 507 284	.919 925 678	.976 118 329
.467	.740 470 047	.601 885 607	.626 880 090	.919 633 093	.975 981 837
.468	.737 603 198	.600 545 357	.626 253 524	.919 340 173	.975 844 897
469	.734 751 428	.599 209 304	.625 627 583	.919 046 919	.975 707 508
.470	.731 914 631	.597 877 429	.625 002 268	.918 753 334	.975 569 670
.471	.729 092 703	.596 549 714	.624 377 578	.918 459 418	.975 431 382
472	.726 285 542	.595 226 138	.623 753 513	.918 165 171	.975 292 645
.473	.723 493 044	.593 906 684	.623 130 071	.917 870 595	.975 153 457
.474	.720 715 107	.592 591 333	.622 507 253	.917 575 690	.975 013 820
.475	.717 951 633	.591 280 065	.621 885 056	.917 280 458	.974 873 732
.476	.715 202 520	.589 972 863	.621 263 482	.916 984 900	.974 733 194
.477	.712 467 670	.588 669 708	.620 642 529	.916 689 016	.974 592 206
.478	.709 746 985	.587 370 582	.620 022 197	.916 392 807	.974 450 766
.479	.707 040 367	.586 075 467	.619 402 485	.916 096 275	.974 308 875
.480	.704 347 722	.584 784 344	.618 783 392	.915 799 420	.974 166 533
.481	.701 668 952	.583 497 197	.618 164 918	.915 502 243	.974 023 740
.482	.699 003 964	.582 214 006	.617 547 062	.915 204 746	.973 880 495
.483	.696 352 664	.580 934 755	.616 929 823	.914 906 928	.973 736 798
.484	.693 714 959	.579 659 425	.616 313 202	.914 608 792	.973 592 649
.485	.691 090 756	.578 388 000	.615 697 197	.914 310 337	.973 448 047
.486	.688 479 965	.577 120 462	.615 081 807	.914 011 566	.973 302 994
.487	.685 882 493	.575 856 794	.614 467 033	.913 712 478	.973 157 488
.488	.683 298 254	.574 596 978	.613 852 873	.913 413 075	.973 011 529
.489	.680 727 155	.573 340 998	.613 239 327	.913 113 358	.972 865 117
.490	.678 169 111	.572 088 836	.612 626 394	.912 813 327	.972 718 252
.491	.675 624 033	.570 840 476	.612 014 074	.912 512 984	.972 570 934
.492	.673 091 833	.569 595 902	.611 402 366	.912 212 330	.972 423 162
.493	.670 572 428	.568 355 095	.610 791 269	.911 911 365	.972 274 937
.494	.668 065 730	.567 118 041	.610 180 783	.911 610 089	.972 126 257
.495	.665 571 656	.565 884 722	.609 570 907	.911 308 506	.971 977 124
.496	.663 090 121	.564 655 123	.608 961 641	.911 006 615	.971 827 537
.497	.660 621 043	.563 429 226	.608 352 984	.910 704 417	.971 677 496
.498	.658 164 338	.562 207 017	.607 744 935	.910 401 912	.971 527 000
.499	.655 719 926	.560 988 478	.607 137 494	.910 099 103	.971 376 049
.500	.653 287 724	.559 773 595	.606 530 660	.909 795 990	.971 224 644

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}\,dx$	$\int_x^\infty \frac{e^{-x}}{x}\,dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.500	0.653 287 724	0.559 773 595	0.606 530 660	0.909 795 990	1.971 224 644
.501	.650 867 653	.558 562 351	.605 924 432	.909 492 573	.971 072 784
.502	.648 459 634	.557 354 730	.605 318 811	.909 188 854	.970 920 469
.503	.646 063 586	.556 150 717	.604 713 794	.908 884 833	.970 767 698
.504	.643 679 432	.554 950 296	.604 109 383	.908 580 512	.970 614 473
.505	.641 307 093	.553 753 452	.603 505 575	.908 275 891	.970 460 791
.506	.638 946 493	.552 560 170	.602 902 372	.907 970 971	.970 306 655
.507	.636 597 555	.551 370 434	.602 299 770	.907 665 754	.970 152 062
.508	.634 260 204	.550 184 229	.601 697 772	.907 360 240	.969 997 013
.509	.631 934 363	.549 001 540	.601 096 375	.907 054 428	.969 841 509
.510	.629 619 959	.547 822 352	.600 495 579	.906 748 324	.969 685 548
.511	.627 316 918	.546 646 650	.599 895 383	.906 441 924	.969 529 131
.512	.625 025 166	.545 474 420	.599 295 788	.906 135 231	.969 372 257
.513	.622 744 630	.544 305 646	.598 696 792	.905 828 246	.969 214 927
.514	.620 475 239	.543 140 314	.598 098 394	.905 520 969	.969 057 141
.515	.618 216 919	.541 978 410	.597 500 595	.905 213 401	.968 898 897
.516	.615 969 602	.540 819 919	.596 903 393	.904 905 543	.968 740 196
.517	613 733 216	.539 664 826	.596 306 788	.904 597 396	.968 581 037
.518	.611 507 691	.538 513 118	.595 710 779	.904 288 962	.968 421 424
.519	.609 292 958	.537 364 780	.595 115 366	.903 980 241	.968 261 352
.520	.607 088 948	.536 219 798	.594 520 548	.903 671 233	.968 100 822
.521	.604 895 594	.535 078 158	.593 926 325	.903 361 940	.967 939 835
.522	.602 712 828	.533 939 845	.593 332 695	.903 052 362	.967 778 390
.523	.600 540 580	.532 804 848	.592 739 659	.902 742 501	.967 616 487
.524	.598 378 788	.531 673 150	.592 147 216	.902 432 357	.967 454 127
.525	.596 227 384	.530 544 739	.591 555 364	.902 121 931	.967 291 309
.526	.594 086 301	.529 419 601	.590 964 105	.901 811 224	.967 128 032
.527	.591 955 476	.528 297 723	.590 373 436	.901 500 237	.966 964 297
.528	.589 834 845	.527 179 090	.589 783 358	.901 188 970	.966 800 104
.529	.587 724 341	.526 063 691	.589 193 869	.900 877 426	.966 635 453
.530	.585 623 904	.524 951 510	.588 604 970	.900 565 604	.966 470 343
.531	.583 533 469	.523 842 536	.588 016 659	.900 253 505	.966 304 775
.532	.581 452 976	.522 736 754	.587 428 936	.899 941 130	.966 138 748
.533	.579 382 360	.521 634 152	.586 841 801	.899 628 481	.965 972 262
.534	.577 321 561	.520 534 717	.586 255 252	.899 315 557	.965 805 317
.535	.575 270 519	.519 438 435	.585 669 290	.899 002 360	.965 637 913
.536	.573 229 172	.518 345 294	.585 083 914	.898 688 891	.965 470 051
.537	.571 197 459	.517 255 282	.584 499 122	.898 375 151	.965 301 729
.538	.569 175 324	.516 168 384	.583 914 915	.898 061 139	.965 132 948
.539	.567 162 705	.515 084 590	.583 331 292	.897 746 859	.964 963 707
.540	.565 159 544	.514 003 886	.582 748 252	.897 432 309	.964 794 008
.541	.563 165 784	.512 926 259	.582 165 795	.897 117 491	.964 623 849
.542	.561 181 367	.511 851 607	.581 583 921	.896 802 406	.964 453 230
.543	.559 206 234	.510 780 188	.581 002 627	.896 487 054	.964 282 152
.544	.557 240 330	.509 711 720	.580 421 915	.896 171 437	.964 110 614
.545	.555 283 598	.508 646 280	.579 841 783	.895 855 555	.963 938 616
.546	.553 335 981	.507 583 857	.579 262 231	.895 539 410	.963 766 159
.547	.551 397 425	.506 524 437	.578 683 259	.895 223 001	.963 593 242
.548	.549 467 875	.505 468 009	.578 104 865	.894 906 331	.963 419 864
.549	.547 547 276	.504 414 561	.577 527 049	.894 589 399	.963 246 027
.550	.545 635 574	.503 364 081	.576 949 810	.894 272 206	.963 071 730

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}dx$
.550	0.545 635 574	0.503 364 081	0.576 949 810	0.894 272 206	1.963 071 730
.551	.543 732 715	.502 316 557	.576 373 149	.893 954 754	.962 896 972
.552	.541 838 645	.501 271 978	.575 797 064	.893 637 043	.962 721 755
.553	.539 953 311	.500 230 332	.575 221 555	.893 319 074	.962 546 077
.554	.538 076 660	.499 191 608	.574 646 621	.893 000 848	.962 369 939
.555	.536 208 643	.498 155 792	.574 072 261	.892 682 366	.962 193 341
.556	.534 349 204	.497 122 875	.573 498 476	.892 363 629	.962 016 282
.557	.532 498 294	.496 092 844	.572 925 264	.892 044 636	.961 838 763
.558	.530 655 861	.495 065 689	.572 352 625	.891 725 390	.961 660 783
.559	.528 821 855	.494 041 398	.571 780 559	.891 405 891	.961 482 342
.560	.526 996 226	.493 019 959	.571 209 064	.891 086 140	.961 303 442
.561	.525 178 925	.492 001 361	.570 638 140	.890 766 137	.961 124 080
.562	.523 369 900	.490 985 594	.570 067 787	.890 445 884	.960 944 258
.563	.521 569 102	.489 972 647	.569 498 005	.890 125 381	.960 763 975
.564	.519 776 484	.488 962 507	.568 928 791	.889 804 629	.960 583 232
.565	.517 991 997	.487 955 165	.568 360 147	.889 483 630	.960 402 027
.566	.516 215 594	.486 950 609	.567 792 071	.889 162 383	.960 220 362
.567	.514 447 225	.485 948 829	.567 224 562	.888 840 888	.960 038 236
.568	.512 686 843	.484 949 814	.566 657 621	.888 519 150	.959 855 649
.569	.510 934 404	.483 953 552	.566 091 247	.888 197 167	.959 672 601
.570	.509 189 858	.482 960 034	.565 525 439	.887 874 939	.959 489 093
.571	.507 453 161	.481 969 249	.564 960 196	.887 552 468	.959 305 123
.572	.505 724 265	.480 981 186	.564 395 518	.887 229 754	.959 120 692
.573	.504 003 126	.479 995 835	.563 831 405	.886 906 800	.958 935 801
.574	.502 289 698	.479 013 185	.563 267 855	.886 583 604	.958 750 448
.575	.500 583 937	.478 033 226	.562 704 869	.886 260 168	.958 564 634
.576	.498 885 798	.477 055 947	.562 142 445	.885 936 494	.958 378 359
.577	.497 195 236	.476 081 339	.561 580 584	.885 612 580	.958 191 623
.578	.495 512 208	.475 109 390	.561 019 284	.885 288 429	.958 004 426
.579	.493 836 670	.474 140 092	.560 458 545	.884 964 042	.957 816 768
.580	.492 168 578	.473 173 433	.559 898 367	.884 639 419	.957 628 649
.581	.490 507 890	.472 209 404	.559 338 748	.884 314 560	.957 440 068
.582	.488 854 563	.471 247 995	.558 779 689	.883 989 468	.957 251 027
583	.487 208 554	.470 289 196	.558 221 188	.883 664 140	.957 061 524
.584	.485 569 823	.469 332 996	.557 663 246	.883 338 582	.956 871 560
.585	.483 938 325	.468 379 387	.557 105 862	.883 012 791	.956 681 135
.586	.482 314 022	.467 428 358	.556 549 034	.882 686 769	.956 490 249
.587	.480 696 870	.466 479 899	.555 992 764	.882 360 515	.956 298 902
.588	.479 086 830	.465 534 001	.555 437 049	.882 034 032	.956 107 094
.589	.477 483 861	.464 590 654	.554 881 889	.881 707 322	.955 914 824
.590	.475 887 922	.463 649 849	.554 327 285	.881 380 383	.955 722 093
.591	.474 298 973	.462 711 576	.553 773 235	.881 053 216	.955 528 901
.592	.472 716 976	.461 775 825	.553 219 738	.880 725 823	.955 335 248
.593	.471 141 890	.460 842 587	.552 666 795	.880 398 204	.955 141 134
.594	.469 573 676	.459 911 853	.552 114 404	.880 070 360	.954 946 559
.595	.468 012 296	.458 983 613	.551 562 566	.879 742 292	.954 751 522
.596	.466 457 711	.458 057 858	.551 011 279	.879 414 001	.954 556 025
.597	.464 909 882	.457 134 579	.550 460 543	.879 085 487	.954 360 066
.598	.463 368 772	.456 213 766	.549 910 358	.878 756 752	.954 163 647
.599	.461 834 343	.455 295 410	.549 360 722	.878 427 795	.953 966 766
.600	.460 306 557	.454 379 503	.548 811 636	.878 098 618	.953 769 424

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}dx$	$\int_x^\infty xe^{-x}dx$	$\int_x^\infty x^2e^{-x}dx$
.600	0.460 306 557	0.454 379 503	0.548 811 636	0.878 098 618	1.953 769 424
.601	.458 785 377	.453 466 035	.548 263 099	.877 769 221	.953 571 622
.602	.457 270 767	.452 554 997	.547 715 110	.877 439 606	.953 373 358
.603	.455 762 688	.451 646 381	.547 167 668	.877 109 772	.953 174 634
.604	.454 261 106	.450 740 176	.546 620 774	.876 779 722	.952 975 448
.605	.452 765 983	.449 836 375	.546 074 427	.876 449 455	.952 775 802
.606	.451 277 285	.448 934 968	.545 528 625	.876 118 972	.952 575 694
.607	.449 794 973	.448 035 948	.544 983 369	.875 788 274	.952 375 126
.608	.448 319 015	.447 139 304	.544 438 658	.875 457 362	.952 174 097
.609	.446 849 375	.446 245 028	.543 894 492	.875 126 237	.951 972 607
.610	.445 386 018	.445 353 112	.543 350 869	.874 794 899	.951 770 657
.611	.443 928 908	.444 463 547	.542 807 790	.874 463 349	.951 568 246
.612	.442 478 011	.443 576 324	.542 265 253	.874 131 588	.951 365 374
.613	.441 033 294	.442 691 435	.541 723 259	.873 799 617	.951 162 041
.614	.439 594 722	.441 808 872	.541 181 807	.873 467 436	.950 958 248
.615	.438 162 262	.440 928 625	.540 640 895	.873 135 046	.950 753 994
.616	.436 735 879	.440 050 687	.540 100 525	.872 802 448	.950 549 280
.617	.435 315 540	.439 175 050	.539 560 694	.872 469 642	.950 344 106
.618	.433 901 214	.438 301 704	.539 021 403	.872 136 630	.950 138 471
.619	.432 492 866	.437 430 641	.538 482 651	.871 803 412	.949 932 375
.620	.431 090 465	.436 561 854	.537 944 438	.871 469 989	.949 725 820
.621	.429 693 978	.435 695 333	.537 406 762	.871 136 361	.949 518 804
.622	.428 303 372	.434 831 072	.536 869 624	.870 802 530	.949 311 327
.623	.426 918 615	.433 969 062	.536 333 023	.870 468 496	.949 103 391
.624	.425 539 677	.433 109 294	.535 796 958	.870 134 259	.948 894 995
.625	.424 166 525	.432 251 761	.535 261 429	.869 799 821	.948 686 138
.626	.422 799 127	.431 396 455	.534 726 435	.869 465 183	.948 476 822
.627	.421 437 455	.430 543 367	.534 191 975	.869 130 344	.948 267 045
.628	.420 081 476	.429 692 490	.533 658 051	.868 795 305	.948 056 809
.629	.418 731 158	.428 843 817	.533 124 659	.868 460 070	.947 846 113
.630	.417 386 473	.427 997 338	.532 591 801	.868 124 636	.947 634 957
.631	.416 047 389	.427 153 047	.532 059 475	.867 789 004	.947 423 342
.632	.414 713 878	.426 310 935	.531 527 682	.867 453 177	.947 211 266
.633	.413 385 908	.425 470 995	.530 996 420	.867 117 154	.946 998 732
.634	.412 063 451	.424 633 219	.530 465 689	.866 780 936	.946 785 738
.635	.410 746 477	.423 797 599	.529 935 488	.866 444 523	.946 572 284
.636	.409 434 956	.422 964 128	.529 405 818	.866 107 918	.946 358 371
.637	.408 128 861	.422 132 798	.528 876 677	.865 771 118	.946 143 999
.638	.406 828 160	.421 303 602	.528 348 064	.865 434 129	.945 929 168
.639	.405 532 827	.420 476 532	.527 819 980	.865 096 948	.945 713 877
.640	.404 242 832	.419 651 581	.527 292 424	.864 759 575	.945 498 128
.641	.402 958 147	.418 828 741	.526 765 395	.864 422 014	.945 281 919
.642	.401 678 745	.418 008 004	.526 238 893	.864 084 262	.945 065 252
.643	.400 404 596	.417 189 365	.525 712 917	.863 746 323	.944 848 126
.644	.399 135 675	.416 372 814	.525 187 467	.863 408 196	.944 630 541
.645	.397 871 953	.415 558 345	.524 662 542	.863 069 882	.944 412 498
.646	.396 613 402	.414 745 951	.524 138 142	.862 731 381	.944 193 996
.647	.395 359 995	.413 935 624	.523 614 266	.862 392 695	.943 975 035
.648	.394 111 706	.413 127 357	.523 090 913	.862 053 825	.943 755 616
.649	.392 868 507	.412 321 144	.522 568 084	.861 714 770	.943 535 739
.650	.391 630 373	.411 516 976	.522 045 777	.861 375 532	.943 315 404

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.650	0.391 630 373	0.411 516 976	0.522 045 777	0.861 375 532	1.943 315 404
.651	.390 397 276	.410 714 847	.521 523 992	.861 036 111	.943 094 611
.652	.389 169 190	.409 914 750	.521 002 729	.860 696 508	.942 873 359
.653	.387 946 089	.409 116 677	.520 481 986	.860 356 723	.942 651 650
.654	.386 727 948	.408 320 622	.519 961 764	.860 016 758	.942 429 483
.655	.385 514 740	.407 526 577	.519 442 063	.859 676 614	.942 206 858
.656	.384 306 439	.406 734 537	.518 922 880	.859 336 290	.941 983 776
.657	.383 103 021	.405 944 493	.518 404 217	.858 995 787	.941 760 236
.658	.381 904 460	.405 156 439	.517 886 072	.858 655 107	.941 536 238
.659	.380 710 730	.404 370 369	.517 368 444	.858 314 249	.941 311 784
.660	.379 521 808	.403 586 275	.516 851 334	.857 973 215	.941 086 872
.661	.378 337 668	.402 804 150	.516 334 741	.857 632 006	.940 861 503
.662	.377 158 284	.402 023 989	.515 818 665	.857 290 621	.940 635 677
.663	.375 983 635	.401 245 783	.515 303 104	.856 949 062	.940 409 394
.664	.374 813 693	.400 469 528	.514 788 058	.856 607 329	.940 182 654
.665	.373 648 436	.399 695 215	.514 273 528	.856 265 424	.939 955 458
.666	.372 487 840	.398 922 838	.513 759 511	.855 923 346	.939 727 805
.667	.371 331 880	.398 152 391	.513 246 009	.855 581 096	.939 499 696
.668	.370 180 533	.397 383 867	.512 733 019	.855 238 676	.939 271 132
.669	.369 033 775	.396 617 260	.512 220 542	.854 896 085	.939 042 108
.670	.367 891 583	.395 852 563	.511 708 578	.854 553 325	.938 812 630
.671	.366 753 933	.395 089 770	.511 197 125	.854 210 396	.938 582 696
.672	.365 620 804	.394 328 874	.510 686 183	.853 867 299	.938 352 307
.673	.364 492 171	.393 569 868	.510 175 752	.853 524 033	.938 121 461
.674	.363 368 012	.392 812 747	.509 665 832	.853 180 602	.937 890 160
.675	.362 248 303	.392 057 505	.509 156 421	.852 837 005	.937 658 403
.676	.361 133 024	.391 304 134	.508 647 519	.852 493 241	.937 426 191
.677	.360 022 151	.390 552 628	.508 139 125	.852 149 313	.937 193 524
.678	.358 915 661	.389 802 982	.507 631 240	.851 805 220	.936 960 401
.679	.357 813 534	.389 055 189	.507 123 863	.851 460 966	.936 726 824
.680	.356 715 746	.388 309 243	.506 616 992	.851 116 547	.936 492 792
.681	.355 622 277	.387 565 137	.506 110 629	.850 771 967	.936 258 305
.682	.354 533 103	.386 822 866	.505 604 771	.850 427 225	.936 023 363
.683	.353 448 205	.386 082 423	.505 099 419	.850 082 322	.935 787 967
.684	.352 367 560	.385 343 802	.504 594 572	.849 737 259	.935 552 116
.685	.351 291 147	.384 606 998	.504 090 230	.849 392 037	.935 315 812
.686	.350 218 945	.383 872 004	.503 586 391	.849 046 656	.935 079 053
.687	.349 150 934	.383 138 814	.503 083 057	.848 701 116	.934 841 840
.688	.348 087 090	.382 407 423	.502 580 225	.848 355 420	.934 604 174
.689	.347 027 396	.381 677 823	.502 077 896	.848 009 565	.934 366 054
.690	.345 971 829	.380 950 010	.501 576 069	.847 663 557	.934 127 480
.691	.344 920 369	.380 223 978	.501 074 744	.847 317 392	.933 888 453
.692	.343 872 996	.379 499 720	.500 573 919	.846 971 072	.933 648 973
.693	.342 829 689	.378 777 231	.500 073 596	.846 624 598	.933 409 039
.694	.341 790 430	.378 056 504	.499 573 772	.846 277 970	.933 168 653
.695	.340 755 196	.377 337 535	.499 074 448	.845 931 189	.932 927 814
.696	.339 723 969	.376 620 317	.498 575 623	.845 584 257	.932 686 522
.697	.338 696 729	.375 904 844	.498 077 297	.845 237 172	.932 444 778
.698	.337 673 456	.375 191 112	.497 579 468	.844 889 937	.932 202 581
.699	.336 654 131	.374 479 113	.497 082 137	.844 542 552	.931 959 933
.700	.335 638 734	.373 768 843	.496 585 304	.844 195 016	.931 716 832

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.700	0.335 638 734	0.373 768 843	0.496 585 304	0.844 195 016	1.931 716 832
.701	.334 627 246	.373 060 296	.496 088 967	.843 847 332	.931 473 279
.702	.333 619 647	.372 353 467	.495 593 126	.843 499 500	.931 229 275
.703	.332 615 920	.371 648 348	.495 097 780	.843 151 520	.930 984 819
.704	.331 616 044	.370 944 936	.494 602 930	.842 803 393	.930 739 911
.705	.330 620 002	.370 243 224	.494 108 574	.842 455 119	.930 494 552
.706	.329 627 773	.369 543 208	.493 614 713	.842 106 700	.930 248 743
.707	.328 639 342	.368 844 880	.493 121 345	.841 758 134	.930 002 482
.708	.327 654 686	.368 148 237	.492 628 470	.841 409 425	.929 755 770
.709	.326 673 790	.367 453 273	.492 136 088	.841 060 573	.929 508 608
.710	.325 696 635	.366 759 981	.491 644 197	.840 711 578	.929 260 995
.711	.324 723 202	.366 068 358	.491 152 799	.840 362 438	.929 012 932
.712	.323 753 473	.365 378 397	.490 661 892	.840 013 159	.928 764 419
.713	.322 787 433	.364 690 092	.490 171 475	.839 663 737	.928 515 456
.714	.321 825 059	.364 003 440	.489 681 549	.839 314 174	.928 266 043
.715	.320 866 339	.363 318 433	.489 192 112	.838 964 472	.928 016 181
.716	.319 911 251	.362 635 068	.488 703 164	.838 614 630	.927 765 869
.717	.318 959 779	.361 953 339	.488 214 705	.838 264 648	.927 515 108
.718	.318 011 906	.361 273 240	.487 726 735	.837 914 530	.927 263 897
.719	.317 067 614	.360 594 767	.487 239 252	.837 564 274	.927 012 238
.720	.316 126 886	.359 917 914	.486 752 256	.837 213 880	.926 760 130
.721	.315 189 705	.359 242 676	.486 265 747	.836 863 351	.926 507 573
.722	.314 256 056	.358 569 047	.485 779 724	.836 512 685	.926 254 568
.723	.313 325 918	.357 897 024	.485 294 187	.836 161 885	.926 001 115
.724	.312 399 278	.357 226 600	.484 809 136	.835 810 950	.925 747 214
.725	.311 476 118	.356 557 770	.484 324 569	.835 459 882	.925 492 864
.726	.310 556 421	.355 890 530	.483 840 486	.835 108 680	.925 238 068
.727	.309 640 170	.355 224 875	.483 356 888	.834 757 345	.924 982 823
.728	.308 727 351	.354 560 798	.482 873 773	.834 405 878	.924 727 131
.729	.307 817 945	.353 898 297	.482 391 140	.834 054 281	.924 470 992
.730	.306 911 937	.353 237 364	.481 908 990	.833 702 553	.924 214 407
.731	.306 009 312	.352 577 996	.481 427 322	.833 350 694	.923 957 374
.732	.305 110 051	.351 920 188	.480 946 135	.832 998 706	.923 699 895
.733	.304 214 142	.351 263 934	.480 465 430	.832 646 589	.923 441 969
.734	.303 321 566	.350 609 230	.479 985 204	.832 294 344	.923 183 597
.735	.302 432 309	.349 956 071	.479 505 459	.831 941 971	.922 924 779
.736	.301 546 354	.349 304 452	.479 026 193	.831 589 471	.922 665 515
.737	.300 663 687	.348 654 368	.478 547 406	.831 236 845	.922 405 806
.738	.299 784 292	.348 005 814	.478 069 098	.830 884 093	.922 145 651
.739	.298 908 153	.347 358 786	.477 591 268	.830 531 215	.921 885 051
.740	.298 035 255	.346 713 279	.477 113 916	.830 178 213	.921 624 006
.741	.297 165 584	.346 069 288	.476 637 040	.829 825 087	.921 362 516
.742	.296 299 124	.345 426 808	.476 160 641	.829 471 837	.921 100 582
.743	.295 435 860	.344 785 834	.475 684 719	.829 118 465	.920 838 202
.744	.294 575 776	.344 146 363	.475 209 272	.828 764 970	.920 575 379
.745	.293 718 860	.343 508 388	.474 734 300	.828 411 352	.920 312 112
.746	.292 865 094	.342 871 907	.474 259 803	.828 057 616	.920 048 400
.747	.292 014 466	.342 236 913	.473 785 780	.827 703 757	.919 784 245
.748	.291 166 961	.341 603 402	.473 312 231	.827 349 780	.919 519 647
.749	.290 322 563	.340 971 370	.472 839 156	.826 995 683	.919 254 605
.750	.289 481 257	.340 340 813	.472 366 553	.826 641 467	.918 989 121

TABLE I.

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}dx$	$\int_x^\infty xe^{-x}dx$	$\int_x^\infty x^2e^{-x}dx$
.750	0.289 481 257	0.340 340 813	0.472 366 553	0.826 641 467	1.918 989 121
.751	.288 643 032	.339 711 725	.471 894 422	.826 287 133	.918 723 193
.752	.287 807 871	.339 084 102	.471 422 764	.825 932 681	.918 456 823
.753	.286 975 761	.338 457 940	.470 951 577	.825 578 114	.918 190 010
.754	.286 146 688	.337 833 233	.470 480 860	.825 223 429	.917 922 755
.755	.285 320 638	.337 209 978	.470 010 615	.824 868 629	.917 655 058
.756	.284 497 595	.336 588 171	.469 540 839	.824 513 713	.917 386 920
.757	.283 677 549	.335 967 805	.469 071 533	.824 158 683	.917 118 339
.758	.282 860 483	.335 348 878	.468 602 696	.823 803 538	.916 849 318
.759	.282 046 385	.334 731 385	.468 134 327	.823 448 282	.916 579 855
.760	.281 235 241	.334 115 321	.467 666 427	.823 092 912	.916 309 952
.761	.280 427 037	.333 500 682	.467 198 994	.822 737 429	.916 039 607
.762	.279 621 760	.332 887 464	.466 732 029	.822 381 835	.915 768 822
.763	.278 819 397	.332 275 662	.466 265 530	.822 026 130	.915 497 597
.764	.278 019 933	.331 665 273	.465 799 498	.821 670 314	.915 225 931
.765	.277 223 357	.331 056 291	.465 333 931	.821 314 388	.914 953 826
.766	.276 429 656	.330 448 712	.464 868 830	.820 958 353	.914 681 281
.767	.275 638 815	.329 842 532	.464 404 193	.820 602 209	.914 408 297
.768	.274 850 821	.329 237 748	.463 940 021	.820 245 957	.914 134 874
.769	.274 065 663	.328 634 354	.463 476 313	.819 889 598	.913 861 011
.770	.273 283 327	.328 032 346	.463 013 068	.819 533 131	.913 586 710
.771	.272 503 800	.327 431 721	.462 550 287	.819 176 558	.913 311 970
.772	.271 727 070	.326 832 474	.462 087 968	.818 819 879	.913 036 792
.773	.270 953 123	.326 234 601	.461 626 111	.818 463 094	.912 761 176
.774	.270 181 948	.325 638 097	.461 164 715	.818 106 205	.912 485 122
.775	.269 413 533	.325 042 959	.460 703 781	.817 749 211	.912 208 631
.776	.268 647 863	.324 449 183	.460 243 307	.817 392 114	.911 931 702
.777	.267 884 927	.323 856 764	.459 783 294	.817 034 913	.911 654 336
.778	.267 124 714	.323 265 698	.459 323 741	.816 677 611	.911 376 533
.779	.266 367 210	.322 675 982	.458 864 647	.816 320 206	.911 098 294
.780	.265 612 404	.322 087 610	.458 406 011	.815 962 700	.910 819 618
.781	.264 860 284	.321 500 580	.457 947 834	.815 605 093	.910 540 505
.782	.264 110 836	.320 914 887	.457 490 115	.815 247 386	.910 260 957
.783	.263 364 049	.320 330 528	.457 032 854	.814 889 579	.909 980 974
.784	.262 619 913	.319 747 497	.456 576 050	.814 531 672	.909 700 553
.785	.261 878 415	.319 165 791	.456 119 702	.814 173 668	.909 419 699
.786	.261 139 542	.318 585 407	.455 663 810	.813 815 565	.909 138 409
.787	.260 403 284	.318 006 340	.455 208 374	.813 457 364	.908 856 684
.788	.259 669 629	.317 428 586	.454 753 393	.813 099 066	.908 574 525
.789	.258 938 564	.316 852 142	.454 298 867	.812 740 673	.908 291 931
.790	.258 210 079	.316 277 004	.453 844 795	.812 382 184	.908 008 904
.791	.257 484 162	.315 703 167	.453 391 177	.812 023 599	.907 725 442
.792	.256 760 802	.315 130 628	.452 938 013	.811 664 919	.907 441 547
.793	.256 039 989	.314 559 382	.452 485 301	.811 306 145	.907 157 219
.794	.255 321 708	.313 989 428	.452 033 042	.810 947 277	.906 872 458
.795	.254 605 952	.313 420 759	.451 581 235	.810 588 317	.906 587 263
.796	.253 892 707	.312 853 373	.451 129 879	.810 229 263	.906 301 636
.797	.253 181 962	.312 287 266	.450 678 975	.809 870 118	.906 015 578
.798	.252 473 709	.311 722 433	.450 228 521	.809 510 881	.905 729 086
.799	.251 767 934	.311 158 872	.449 778 518	.809 151 554	.905 442 163
.800	.251 064 627	.310 596 578	.449 328 964	.808 792 135	.905 154 808

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.800	0.251 064 627	0.310 596 578	0.449 328 964	0.808 792 135	1.905 154 808
.801	.250 363 777	.310 035 549	.448 879 860	.808 432 627	.904 867 022
.802	.249 665 373	.309 475 779	.448 431 204	.808 073 030	.904 578 804
.803	.248 969 406	.308 917 265	.447 982 997	.807 713 344	.904 290 156
.804	.248 275 864	.308 360 004	.447 535 238	.807 353 570	.904 001 078
.805	.247 584 737	.307 803 992	.447 087 927	.806 993 708	.903 711 568
.806	.246 896 013	.307 249 225	.446 641 062	.806 633 758	.903 421 629
.807	.246 209 683	.306 695 700	.446 194 644	.806 273 722	.903 131 260
.808	.245 525 736	.306 143 413	.445 748 673	.805 913 600	.902 840 462
.809	.244 844 162	.305 592 361	.445 303 147	.805 553 393	.902 549 234
.810	.244 164 950	.305 042 539	.444 858 066	.805 193 100	.902 257 577
.811	.243 488 091	.304 493 944	.444 413 431	.804 832 723	.901 965 491
.812	.242 813 573	.303 946 574	.443 969 239	.804 472 261	.901 672 977
.813	.242 141 387	.303 400 423	.443 525 492	.804 111 717	.901 380 034
.814	.241 471 523	.302 855 489	.443 082 188	.803 751 088	.901 086 664
.815	.240 803 971	.302 311 768	.442 639 327	.803 390 379	.900 792 866
.816	.240 138 721	.301 769 256	.442 196 909	.803 029 587	.900 498 640
.817	.239 475 762	.301 227 951	.441 754 933	.802 668 714	.900 203 987
.818	.238 815 085	.300 687 848	.441 313 399	.802 307 760	.899 908 907
.819	.238 156 680	.300 148 944	.440 872 306	.801 946 726	.899 613 400
.820	.237 500 539	.299 611 235	.440 431 655	.801 585 611	.899 317 467
.821	.236 846 649	.299 074 719	.439 991 443	.801 224 418	.899 021 108
.822	.236 195 002	.298 539 392	.439 551 671	.800 863 145	.898 724 322
.823	.235 545 589	.298 005 249	.439 112 340	.800 501 795	.898 427 112
.824	.234 898 399	.297 472 289	.438 673 447	.800 140 367	.898 129 475
.825	.234 253 423	.296 940 507	.438 234 992	.799 778 861	.897 831 414
.826	.233 610 653	.296 409 900	.437 796 977	.799 417 279	.897 532 927
.827	.232 970 077	.295 880 465	.437 359 398	.799 055 621	.897 234 018
.828	.232 331 688	.295 352 198	.436 922 258	.798 693 887	.896 934 683
.829	.231 695 475	.294 825 096	.436 485 554	.798 332 078	.896 634 924
.830	.231 061 431	.294 299 155	.436 049 286	.797 970 194	.896 334 741
.831	.230 429 544	.293 774 373	.435 613 455	.797 608 236	.896 034 135
.832	.229 799 806	.293 250 746	.435 178 059	.797 246 205	.895 733 106
.833	.229 172 208	.292 728 271	.434 743 099	.796 884 100	.895 431 654
.834	.228 546 741	.292 206 944	.434 308 573	.796 521 923	.895 129 779
.835	.227 923 394	.291 686 763	.433 874 481	.796 159 673	.894 827 482
.836	.227 302 162	.291 167 723	.433 440 824	.795 797 352	.894 524 763
.837	.226 683 033	.290 649 822	.433 007 600	.795 434 959	.894 221 622
.838	.226 065 999	.290 133 056	432 574 808	.795 072 498	.893 918 060
.839	.225 451 051	.289 617 423	.432 142 450	.794 709 965	.893 614 076
.840	.224 838 181	.289 102 918	.431 710 523	.794 347 363	.893 309 672
.841	.224 227 380	.288 589 539	.431 279 029	.793 984 692	.893 004 846
.842	.223 618 638	.288 077 283	.430 847 965	.793 621 952	.892 699 601
.843	.223 011 946	.287 566 147	.430 417 333	.793 259 144	.892 393 935
.844	.222 407 299	.287 056 126	.429 987 130	.792 896 268	.892 087 850
.845	.221 804 684	.286 547 219	.429 557 358	.792 533 326	.891 781 344
.846	.221 204 096	.286 039 421	.429 128 016	.792 170 317	.891 474 420
.847	.220 605 524	.285 532 731	.428 699 102	.791 807 241	.891 167 077
.848	.220 008 961	.285 027 144	.428 270 617	.791 444 101	.890 859 315
.849	.219 414 399	.284 522 657	.427 842 561	.791 080 894	.890 551 135
.850	.218 821 828	.284 019 268	.427 414 932	.790 717 624	.890 242 537

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}\,dx$	$\int_x^\infty \frac{e^{-x}}{x}\,dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.850	0.218 821 828	0.284 019 268	0.427 414 932	0.790 717 624	1.890 242 537
.851	.218 231 241	.283 516 974	.426 987 731	.790 354 290	.889 933 520
.852	.217 642 628	.283 015 771	.426 560 956	.789 990 891	.889 624 087
.853	.217 055 984	.282 515 656	.426 134 609	.789 627 430	.889 314 236
.854	.216 471 297	.282 016 627	.425 708 687	.789 263 906	.889 003 968
.855	.215 888 562	.281 518 679	.425 283 191	.788 900 319	.888 693 284
.856	.215 307 769	.281 021 811	.424 858 120	.788 536 672	.888 382 183
.857	.214 728 911	.280 526 019	.424 433 475	.788 172 963	.888 070 666
.858	.214 151 979	.280 031 300	.424 009 253	.787 809 193	.887 758 734
.859	.213 576 965	.279 537 652	.423 585 456	.787 445 363	.887 446 385
.860	.213 003 863	.279 045 070	.423 162 082	.787 081 473	.887 133 622
.861	.212 432 663	.278 553 553	.422 739 132	.786 717 524	.886 820 444
.862	.211 863 358	.278 063 097	.422 316 604	.786 353 516	.886 506 852
.863	.211 295 940	.277 573 699	.421 894 498	.785 989 451	.886 192 845
.864	.210 730 402	.277 085 356	.421 472 815	.785 625 327	.885 878 424
.865	.210 166 735	.276 598 066	.421 051 553	.785 261 145	.885 563 589
.866	.209 604 931	.276 111 826	.420 630 712	.784 896 908	.885 248 341
.867	.209 044 984	.275 626 632	.420 210 291	.784 532 613	.884 932 680
.868	.208 486 885	.275 142 482	.419 790 291	.784 168 263	.884 616 607
.869	.207 930 628	.274 659 372	.419 370 710	.783 803 858	.884 300 120
.870	.207 376 204	.274 177 301	.418 951 549	.783 439 397	.883 983 222
.871	.206 823 606	.273 696 264	.418 532 807	.783 074 882	.883 665 912
.872	.206 272 827	.273 216 260	.418 114 483	.782 710 313	.883 348 190
.873	.205 723 858	.272 737 285	.417 696 578	.782 345 690	.883 030 056
.874	.205 176 693	.272 259 337	.417 279 090	.781 981 015	.882 711 512
.875	.204 631 325	.271 782 412	.416 862 020	.781 616 287	.882 392 558
.876	.204 087 744	.271 306 509	.416 445 366	.781 251 507	.882 073 193
.877	.203 545 947	.270 831 623	.416 029 129	.780 886 675	.881 753 417
.878	.203 005 924	.270 357 752	.415 613 308	.780 521 792	.881 433 232
.879	.202 467 667	.269 884 895	.415 197 902	.780 156 858	.881 112 638
.880	.201 931 172	.269 413 046	.414 782 912	.779 791 874	.880 791 635
.881	.201 396 428	.268 942 205	.414 368 336	.779 426 840	.880 470 222
.882	.200 863 431	.268 472 368	.413 954 175	.779 061 757	.880 148 402
.883	.200 332 173	.268 003 532	.413 540 428	.778 696 625	.879 826 173
.884	.199 802 645	.267 535 696	.413 127 094	.778 331 445	.879 503 536
.885	.199 274 844	.267 068 855	.412 714 173	.777 966 217	.879 180 492
.886	.198 748 760	.266 603 007	.412 301 665	.777 600 941	.878 857 040
.887	.198 224 386	.266 138 150	.411 889 570	.777 235 618	.878 533 181
.888	.197 701 717	.265 674 281	.411 477 886	.776 870 249	.878 208 916
.889	.197 180 744	.265 211 398	.411 066 614	.776 504 834	.877 884 245
.890	.196 661 462	.264 749 496	.410 655 753	.776 139 373	.877 559 167
.891	.196 143 863	.264 288 575	.410 245 302	.775 773 867	.877 233 684
.892	.195 627 941	.263 828 631	.409 835 262	.775 408 316	.876 907 795
.893	.195 113 689	.263 369 661	.409 425 632	.775 042 721	.876 581 502
.894	.194 601 101	.262 911 663	.409 016 411	.774 677 082	.876 254 803
.895	.194 090 169	.262 454 634	.408 607 599	.774 311 399	.875 927 701
.896	.193 580 887	.261 998 572	.408 199 195	.773 945 674	.875 600 194
.897	.193 073 248	.261 543 475	.407 791 200	.773 579 907	.875 272 283
.898	.192 567 246	.261 089 338	.407 383 613	.773 214 097	.874 943 969
.899	.192 062 874	.260 636 161	.406 976 433	.772 848 246	.874 615 252
.900	.191 560 127	.260 183 939	.406 569 660	.772 482 353	.874 286 132

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.900	0.191 560 127	0.260 183 939	0.406 569 660	0.772 482 353	1.874 286 132
.901	.191 058 996	.259 732 672	.406 163 293	.772 116 421	.873 956 609
.902	.190 559 478	.259 282 355	.405 757 333	.771 750 447	.873 626 685
.903	.190 061 563	.258 832 987	.405 351 778	.771 384 434	.873 296 357
.904	.189 565 246	.258 384 565	.404 946 629	.771 018 382	.872 965 629
.905	.189 070 521	.257 937 087	.404 541 885	.770 652 291	.872 634 500
.906	.188 577 382	.257 490 549	.404 137 545	.770 286 162	.872 302 969
.907	.188 085 822	.257 044 950	.403 733 610	.769 919 994	.871 971 039
.908	.187 595 834	.256 600 287	.403 330 078	.769 553 789	.871 638 707
.909	.187 107 414	.256 156 557	.402 926 950	.769 187 547	.871 305 976
.910	.186 620 554	.255 713 758	.402 524 224	.768 821 268	.870 972 846
.911	.186 135 249	.255 271 887	.402 121 901	.768 454 953	.870 639 316
.912	.185 651 492	.254 830 942	.401 719 980	.768 088 602	.870 305 387
.913	.185 169 277	.254 390 921	.401 318 461	.767 722 216	.869 971 060
.914	.184 688 598	.253 951 821	.400 917 343	.767 355 795	.869 636 334
.915	.184 209 449	.253 513 640	.400 516 626	.766 989 339	.869 301 210
.916	.183 731 824	.253 076 374	.400 116 310	.766 622 849	.868 965 689
.917	.183 255 717	.252 640 023	.399 716 393	.766 256 326	.868 629 770
.918	.182 781 123	.252 204 582	.399 316 877	.765 889 770	.868 293 455
.919	.182 308 033	.251 770 051	.398 917 759	.765 523 180	.867 956 743
.920	.181 836 446	.251 336 425	.398 519 041	.765 156 559	.867 619 634
.921	.181 366 352	.250 903 704	.398 120 721	.764 789 905	.867 282 130
.922	.180 897 747	.250 471 884	.397 722 800	.764 423 221	.866 944 230
.923	.180 430 624	.250 040 964	.397 325 276	.764 056 505	.866 605 934
.924	.179 964 979	.249 610 940	.396 928 149	.763 689 758	.866 267 244
.925	.179 500 804	.249 181 811	.396 531 419	.763 322 982	.865 928 159
.926	.179 038 095	.248 753 574	.396 135 086	.762 956 175	.865 588 680
.927	.178 576 846	.248 326 227	.395 739 149	.762 589 340	.865 248 806
.928	.178 117 051	.247 899 767	.395 343 607	.762 222 475	.864 908 539
.929	.177 658 704	.247 474 193	.394 948 461	.761 855 581	.864 567 879
.930	.177 201 800	.247 049 501	.394 553 710	.761 488 661	.864 226 826
.931	.176 746 334	.246 625 689	.394 159 354	.761 121 712	.863 885 390
.932	.176 292 299	.246 202 756	.393 765 392	.760 754 736	.863 543 542
.933	.175 839 691	.245 780 698	.393 371 823	.760 387 734	.863 201 312
.934	.175 388 503	.245 359 514	.392 978 648	.760 020 705	.862 858 691
.935	.174 938 729	.244 939 202	.392 585 866	.759 653 649	.862 515 678
.936	.174 490 366	.244 519 758	.392 193 476	.759 286 569	.862 172 274
.937	.174 043 406	.244 101 181	.391 801 478	.758 919 464	.861 828 480
.938	.173 597 846	.243 683 468	.391 409 873	.758 552 333	.861 484 295
.939	.173 153 680	.243 266 617	.391 018 659	.758 185 179	.861 139 721
.940	.172 710 900	.242 850 627	.390 627 835	.757 818 001	.860 794 757
.941	.172 269 505	.242 435 493	.390 237 403	.757 450 799	.860 449 403
.942	.171 829 485	.242 021 216	.389 847 360	.757 083 574	.860 103 661
.943	.171 390 839	.241 607 791	.389 457 708	.756 716 326	.859 757 530
.944	.170 953 558	.241 195 218	.389 068 445	.756 349 057	.859 411 011
.945	.170 517 640	.240 783 493	.388 679 571	.755 981 765	.859 064 105
.946	.170 083 078	.240 372 615	.388 291 086	.755 614 453	.858 716 810
.947	.169 649 867	.239 962 581	.387 902 989	.755 247 119	.858 369 129
.948	.169 218 003	.239 553 389	.387 515 279	.754 879 764	.858 021 061
.949	.168 787 478	.239 145 038	.387 127 958	.754 512 390	.857 672 606
.950	.168 358 290	.238 737 524	.386 741 023	.754 144 996	.857 323 765

TABLE I

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
.950	0.168 358 290	0.238 737 524	0.386 741 023	0.754 144 996	1.857 323 765
.951	.167 930 433	.238 330 845	.386 354 476	.753 777 582	.856 974 539
.952	.167 503 902	.237 925 000	.385 968 314	.753 410 150	.856 624 927
.953	.167 078 690	.237 519 987	.385 582 539	.753 042 699	.856 274 929
.954	.166 654 795	.237 115 802	.385 197 149	.752 675 230	.855 924 548
.955	.166 232 209	.236 712 445	.384 812 145	.752 307 743	.855 573 781
.956	.165 810 930	.236 309 912	.384 427 525	.751 940 238	.855 222 631
.957	.165 390 951	.235 908 202	.384 043 289	.751 572 717	.854 871 097
.958	.164 972 267	.235 507 313	.383 659 438	.751 205 180	.854 519 180
.959	.164 554 874	.235 107 243	.383 275 970	.750 837 625	.854 166 880
.960	.164 138 768	.234 707 988	.382 892 886	.750 470 057	.853 814 197
.961	.163 723 943	.234 309 548	.382 510 184	.750 102 472	.853 461 132
.962	.163 310 393	.233 911 920	.382 127 865	.749 734 872	.853 107 684
.963	.162 898 115	.233 515 103	.381 745 929	.749 367 258	.852 753 856
.964	.162 487 104	.233 119 093	.381 364 373	.748 999 630	.852 399 646
.965	.162 077 353	.232 723 890	.380 983 200	.748 631 986	.852 045 055
.966	.161 668 861	.232 329 490	.380 602 407	.748 264 332	.851 690 084
.967	.161 261 620	.231 935 893	.380 221 995	.747 896 664	.851 334 732
.968	.160 855 627	.231 543 095	.379 841 963	.747 528 983	.850 979 001
.969	.160 450 878	.231 151 094	.379 462 311	.747 161 290	.850 622 890
.970	.160 047 366	.230 759 890	.379 083 038	.746 793 585	.850 266 401
.971	.159 645 088	.230 369 479	.378 704 145	.746 425 869	.849 909 532
.972	.159 244 039	.229 979 860	.378 325 630	.746 058 142	.849 552 285
.973	.158 844 214	.229 591 031	.377 947 493	.745 690 404	.849 194 660
.974	.158 445 609	.229 202 989	.377 569 735	.745 322 656	.848 836 658
.975	.158 048 219	.228 815 733	.377 192 354	.744 954 898	.848 478 278
.976	.157 652 050	.228 429 251	.376 815 350	.744 587 130	.848 119 521
.977	.157 257 067	.228 043 570	.376 438 723	.744 219 355	.847 760 387
.978	.156 863 297	.227 658 658	.376 062 472	.743 851 570	.847 400 878
.979	.156 470 723	.227 274 525	.375 686 598	.743 483 777	.847 040 992
.980	.156 079 342	.226 891 167	.375 311 099	.743 115 976	.846 680 731
.981	.155 689 149	.226 508 583	.374 935 975	.742 748 167	.846 320 094
.982	.155 300 140	.226 126 771	.374 561 227	.742 380 352	.845 959 083
.983	.154 912 310	.225 745 729	.374 186 853	.742 012 529	.845 597 698
.984	.154 525 657	.225 365 454	.373 812 853	.741 644 700	.845 235 938
.985	.154 140 173	.224 985 946	.373 439 227	.741 276 865	.844 873 805
.986	.153 765 998	.224 607 201	.373 065 974	.740 909 025	.844 511 298
.987	.153 372 701	.224 229 219	.372 693 095	.740 541 179	.844 148 419
.988	.152 990 703	.223 851 997	.372 320 588	.740 173 329	.843 785 166
.989	.152 609 860	.223 475 533	.371 948 454	.739 805 474	.843 421 542
.990	.152 230 165	.223 099 826	.371 576 691	.739 437 615	.843 057 545
.991	.151 851 615	.222 724 873	.371 205 300	.739 069 752	.842 693 177
.992	.151 474 207	.222 350 672	.370 834 280	.738 701 886	.842 328 438
.993	.151 097 935	.221 977 222	.370 463 631	.738 334 017	.841 963 328
.994	.150 722 796	.221 604 521	.370 093 353	.737 966 146	.841 597 847
.995	.150 348 784	.221 232 567	.369 723 445	.737 598 272	.841 231 997
.996	.149 975 897	.220 861 358	.369 353 906	.737 230 396	.840 865 777
.997	.149 604 130	.220 490 892	.368 984 737	.736 862 519	.840 499 187
.998	.149 233 479	.220 121 167	.368 615 936	.736 494 641	.840 132 228
.999	.148 863 939	.219 752 182	.368 247 505	.736 126 762	.839 764 901
1.000	.148 495 507	.219 383 934	.367 879 441	.735 758 882	.839 397 206

TABLE II.

x	$\int_x^\infty \frac{e^{-x}}{x^2}\,dx$	$\int_x^\infty \frac{e^{-x}}{x}\,dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
1.00	0.148 495 507	0.219 383 934	0.367 879 441	0.735 758 882	1.839 397 206
1.01	.144 871 228	.215 741 623	.364 218 980	.732 080 149	.835 700 079
1.02	.141 353 368	.212 171 083	.360 594 940	.728 401 779	.831 966 534
1.03	.137 938 141	.208 670 559	.357 006 961	.724 724 130	.828 196 944
1.04	.134 621 920	.205 238 351	.353 454 682	.721 047 551	.824 391 686
1.05	.131 401 234	.201 872 813	.349 937 749	.717 372 386	.820 551 140
1.06	.128 272 758	.198 572 346	.346 455 810	.713 698 969	.816 675 687
1.07	.125 233 305	.195 335 403	.343 008 517	.710 027 631	.812 765 714
1.08	.122 279 823	.192 160 479	.339 595 526	.706 358 693	.808 821 608
1.09	.119 409 381	.189 046 118	.336 216 494	.702 692 472	.804 843 760
1.10	.116 619 171	.185 990 905	.332 871 084	.699 029 276	.800 832 563
1.11	.113 906 500	.182 993 465	.329 558 961	.695 369 408	.796 788 412
1.12	.111 268 778	.180 052 467	.326 279 795	.691 713 165	.792 711 704
1.13	.108 703 523	.177 166 615	.323 033 256	.688 060 836	.788 602 837
1.14	.106 208 351	.174 334 651	.319 819 022	.684 412 707	.784 462 214
1.15	.103 780 967	.171 555 354	.316 636 769	.680 769 054	.780 290 236
1.16	.101 419 173	.168 827 535	.313 486 181	.677 130 151	.776 087 306
1.17	.099 120 850	.166 150 040	.310 366 941	.673 496 263	.771 853 831
1.18	.096 883 963	.163 521 748	.307 278 739	.669 867 650	.767 590 216
1.19	.094 706 554	.160 941 567	.304 221 264	.666 244 568	.763 296 869
1.20	092 586 740	.158 408 437	.301 194 212	.662 627 266	.758 974 198
1.21	.090 522 708	.155 921 325	.298 197 279	.659 015 988	.754 622 612
1.22	.088 512 714	.153 479 226	.295 230 167	.655 410 971	.750 242 522
1.23	.086 555 078	.151 081 164	.292 292 578	.651 812 448	.745 834 337
1.24	.084 648 181	.148 726 188	.289 384 218	.648 220 648	.741 398 470
1.25	.082 790 464	.146 413 373	.286 504 797	.644 635 793	.736 935 331
1.26	.080 980 428	.144 141 815	.283 654 027	.641 058 100	.732 445 332
1.27	.079 216 622	.141 910 639	.280 831 622	.637 487 781	.727 928 886
1.28	.077 497 652	.139 718 989	.278 037 300	.633 925 045	.723 386 403
1.29	.075 822 172	.137 566 032	.275 270 783	.630 370 093	.718 818 297
1.30	.074 188 883	.135 450 958	.272 531 793	.626 823 124	.714 224 978
1.31	.072 596 534	.133 372 975	.269 820 056	.632 284 330	.709 606 859
1.32	.071 043 915	.131 331 314	.267 135 302	.619 753 901	.704 964 351
1.33	.069 529 860	.129 325 224	.264 477 261	.616 232 019	.700 297 865
1.34	.068 053 243	.127 353 972	.261 845 669	.612 718 864	.695 607 811
1.35	.066 612 979	.125 416 844	.259 240 261	.609 214 613	.690 894 600
1.36	.065 208 014	.123 513 146	.256 660 777	.605 719 434	.686 158 640
1.37	.063 837 335	.121 642 198	.254 106 960	.602 233 494	.681 400 341
1.38	.062 499 961	.119 803 338	.251 578 553	.598 756 956	.676 620 109
1.39	.061 194 948	.117 995 919	.249 075 305	.595 289 978	.671 818 352
1.40	.059 921 376	.116 219 313	.246 596 964	.591 832 713	.666 995 476
1.41	.058 678 362	.114 472 903	.244 143 283	.588 385 312	.662 151 886
1.42	.057 465 049	.112 756 090	.241 714 017	.584 947 921	.657 287 985
1.43	.056 280 610	.111 068 287	.239 308 922	.581 520 681	.652 404 177
1.44	.055 124 243	.109 408 923	.236 927 759	.578 103 731	.647 500 863
1.45	.053 995 172	.107 777 440	.234 570 288	.574 697 206	.642 578 442
1.46	.052 892 650	.106 173 292	.232 236 275	.571 301 236	.637 637 315
1.47	.051 815 949	.104 595 946	.229 925 485	.567 915 948	.632 677 878
1.48	.050 764 367	.103 044 882	.227 637 688	.564 541 467	.627 700 527
1.49	.049 737 223	.101 519 593	.225 372 656	.561 177 912	.622 705 657
1.50	.048 733 858	.100 019 582	.223 130 160	.557 825 400	.617 693 661

TABLE II.

x	$\int_x^\infty \frac{e^{-x}}{x^2}dx$	$\int_x^\infty \frac{e^{-x}}{x}dx$	$\int_x^\infty e^{-x}\,dx$	$\int_x^\infty xe^{-x}\,dx$	$\int_x^\infty x^2e^{-x}\,dx$
1.50	0.048 733 858	0.100 019 582	0.223 130 160	0.557 825 400	1.617 693 661
1.51	.047 753 634	.098 544 365	.220 909 978	.554 484 045	.612 664 930
1.52	.046 795 933	.097 093 466	.218 711 887	.551 153 955	.607 619 854
1.53	.045 860 156	.095 666 424	.216 535 667	.547 835 238	.602 558 820
1.54	.044 945 721	.094 262 786	.214 381 101	.544 527 998	.597 482 215
1.55	.044 052 069	.092 882 108	.212 247 974	.541 232 333	.592 390 424
1.56	.043 178 651	.091 523 959	.210 136 071	.537 948 342	.587 283 827
1.57	.042 324 938	.090 187 917	.208 045 182	.534 676 119	.582 162 807
1.58	.041 490 420	.088 873 566	.205 975 098	.531 415 753	.577 027 742
1.59	.040 674 598	.087 580 504	.203 925 612	.528 167 334	.571 879 008
1.60	.039 876 990	.086 308 334	.201 896 518	.524 930 947	.566 716 980
1.61	.039 097 128	.085 056 670	.199 887 614	.521 706 673	.561 542 030
1.62	.038 334 558	.083 825 133	.197 898 699	.518 494 592	.556 354 529
1.63	.037 588 839	.082 613 354	.195 929 574	.515 294 780	.551 154 845
1.64	.036 859 544	.081 420 970	.193 980 042	.512 107 312	.545 943 345
1.65	.036 146 257	.080 247 627	.192 049 909	.508 932 258	.540 720 392
1.66	.035 448 576	.079 092 978	.190 138 980	.505 769 687	.535 486 348
1.67	.034 766 110	.077 956 684	.188 247 066	.502 619 665	.530 241 572
1.68	.034 098 477	.076 838 413	.186 373 976	.499 482 256	.524 986 422
1.69	.033 445 311	.075 737 839	.184 519 524	.496 357 520	.519 721 252
1.70	.032 806 253	.074 654 644	.182 683 524	.493 245 515	.514 446 414
1.71	.032 180 951	.073 588 518	.180 865 793	.490 146 298	.509 162 260
1.72	.031 569 070	.072 539 155	.179 066 148	.487 059 922	.503 869 137
1.73	.030 970 283	.071 506 255	.177 284 410	.483 986 439	.498 567 390
1.74	.030 384 266	.070 489 527	.175 520 401	.480 925 898	.493 257 360
1.75	.029 810 711	.069 488 685	.173 773 943	.477 878 344	.487 939 391
1.76	.029 249 317	.068 503 447	.172 044 864	.474 843 824	.482 613 818
1.77	.028 699 788	.067 533 539	.170 332 989	.471 822 379	.477 280 979
1.78	.028 161 841	.066 578 691	.168 638 147	.468 814 049	.471 941 205
1.79	.027 635 197	.065 638 641	.166 960 170	.465 818 873	.466 594 826
1.80	.027 119 587	.064 713 129	.165 298 888	.462 836 887	.461 242 172
1.81	.026 614 747	.063 801 903	.163 654 137	.459 868 124	.455 883 566
1.82	.026 120 423	.062 904 715	.162 025 751	.456 912 618	.450 519 333
1.83	.025 636 366	.062 021 321	.160 413 568	.453 970 397	.445 149 791
1.84	.025 162 336	.061 151 483	.158 817 426	.451 041 490	.439 775 258
1.85	.024 698 095	.060 294 968	.157 237 166	.448 125 924	.434 396 050
1.86	.024 243 418	.059 451 545	.155 672 630	.445 223 723	.429 012 478
1.87	.023 798 076	.058 620 994	.154 123 662	.442 334 909	.423 624 852
1.88	.023 361 859	.057 803 091	.152 590 106	.439 459 505	.418 233 479
1.89	.022 934 551	.056 997 623	.151 071 809	.436 597 528	.412 838 663
1.90	.022 515 948	.056 204 378	.149 568 619	.433 748 996	.407 440 707
1.91	.022 105 850	.055 423 148	.148 080 387	.430 913 925	.402 039 908
1 92	.021 704 062	.054 653 731	.146 606 962	.428 092 329	.396 636 564
1.93	.021 310 393	.053 895 927	.145 148 198	.425 284 222	.391 230 968
1.94	.020 924 661	.053 149 540	.143 703 950	.422 489 612	.385 823 410
1.95	.020 546 682	.052 414 380	.142 274 072	.419 708 511	.380 414 180
1.96	.020 176 284	.051 690 257	.140 858 421	.416 940 926	.375 003 502
1.97	.019 813 294	.050 976 988	.139 456 856	.414 186 863	.369 591 839
1.98	.019 457 546	.050 274 392	.138 069 237	.411 446 327	.364 179 292
1.99	.019 108 879	.049 582 290	.136 695 425	.408 719 322	.358 766 198
2.00	.018 767 131	.048 900 511	.135 335 283	.406 005 850	.353 352 832

TABLE III.

x	$\frac{e^{-x}-1}{x}$	x	$\frac{e^{-x}-1}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$
.000	1.000 000 000	.050	0.975 411 510	.100	9.048 374 180	.150	5.738 053 176
.001	0.999 500 167	.051	.974 928 029	.101	8.949 832 009	.151	.694 355 620
.002	.999 000 667	.052	.974 444 868	.102	.853 230 899	.152	.651 238 689
.003	.998 501 499	.053	.973 962 029	.103	.758 514 306	.153	.608 690 992
.004	.998 002 664	.054	.973 479 509	.104	.665 627 860	.154	.566 701 435
.005	.997 504 161	.055	.972 997 310	.105	.574 519 263	.155	.525 259 210
.006	.997 005 991	.056	.972 515 431	.106	.485 138 189	.156	.484 353 784
.007	.996 508 153	.057	.972 033 871	.107	.397 436 196	.157	.443 974 897
.008	.996 010 645	.058	.971 552 630	.108	.311 366 634	.158	.404 112 544
.009	.995 513 470	.059	.971 071 709	.109	.226 884 564	.159	.364 756 975
.010	.995 016 625	.060	.970 591 107	.110	.143 946 685	.160	.325 898 681
.011	.994 520 111	.061	.970 110 823	.111	.062 511 252	.161	.287 528 392
.012	.994 023 928	.062	.969 630 858	.112	7.982 538 013	.162	.249 637 065
.013	.993 528 076	.063	.969 151 211	.113	.903 988 142	.163	.212 215 880
.014	.993 032 553	.064	.968 671 882	.114	.826 824 174	.164	.175 256 231
.015	.992 537 360	.065	.968 192 871	.115	.751 009 947	.165	.138 749 722
.016	.992 042 497	.066	.967 714 177	.116	.676 510 546	.166	.102 688 158
.017	.991 547 963	.067	.967 235 801	.117	.603 292 249	.167	.067 063 541
.018	.991 053 758	.068	.966 757 742	.118	.531 322 480	.168	.031 868 064
.019	.990 559 882	.069	.966 279 999	.119	.460 569 754	.169	4.997 094 103
.020	.990 066 335	.070	.965 802 573	.120	.391 003 639	.170	.962 734 215
.021	989 573 116	.071	.965 325 463	.121	.322 594 707	.171	.928 781 131
.022	.989 080 225	.072	.964 848 669	.122	.255 314 496	.172	.895 227 751
.023	.988 587 662	.073	.964 372 191	.123	.189 135 468	.173	.862 067 138
.024	.988 095 427	.074	.963 896 029	.124	.124 030 975	.174	.829 292 515
.025	.987 603 519	.075	.963 420 182	.125	.059 975 221	.175	.796 897 262
.026	.987 111 938	.076	.962 944 651	.126	6.996 943 228	.176	.764 874 905
.027	.986 620 684	.077	.962 469 434	.127	.934 910 808	.177	.733 219 122
.028	.986 129 757	.078	.961 994 531	.128	.873 854 525	.178	.701 923 727
.029	.985 639 156	.079	.961 519 944	.129	.813 751 671	.179	.670 982 678
.030	.985 148 882	.080	.961 045 670	.130	.754 580 238	.180	.640 390 063
.031	.984 658 933	.081	.960 571 711	.131	.696 318 888	.181	.610 140 103
.032	.984 169 310	.082	.960 098 065	.132	.638 946 932	.182	.580 227 145
.033	.983 680 012	.083	.959 624 732	.133	.582 444 302	.183	.550 645 660
.034	.983 191 040	.084	.959 151 713	.134	.526 791 527	.184	.521 390 238
.035	.982 702 393	.085	.958 679 007	.135	.471 969 716	.185	.492 455 588
.036	.982 214 070	.086	.958 206 614	.136	.417 960 533	.186	.463 836 532
.037	.981 726 072	.087	.957 734 533	.137	.364 746 176	.187	.435 528 002
.038	.981 238 398	.088	.957 262 765	.138	.312 309 360	.188	.407 525 038
.039	.980 751 048	.089	.956 791 308	.139	.260 633 298	.189	.379 822 787
.040	.980 264 021	.090	.956 320 164	.140	.209 701 681	.190	.352 416 494
.041	.979 777 318	.091	.955 849 331	.141	.159 498 665	.191	.325 301 509
.042	.979 290 939	.092	.955 378 809	.142	.110 008 849	.192	.298 473 273
.043	.978 804 882	.093	.954 908 599	.143	.061 217 265	.193	.271 927 327
.044	.978 319 148	.094	.954 438 700	.144	.013 109 362	.194	.245 659 300
.045	.977 833 737	.095	.953 969 111	.145	5.965 670 987	.195	.219 664 913
.046	.977 348 648	.096	.953 499 833	.146	.918 888 378	.196	.193 939 973
.047	.976 863 881	.097	.953 030 865	.147	.872 748 146	.197	.168 480 372
.048	.976 379 436	.098	.952 562 207	.148	.827 237 263	.198	.143 282 087
.049	.975 895 310	.099	.952 093 858	.149	.782 343 053	.199	.118 341 173
.050	.975 411 510	.100	.951 625 820	.150	.738 053 176	.200	.093 653 765

TABLE III.

x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$
.200	4.093 653 765	.250	3.115 203 132	.300	2.469 394 069	.350	2.013 394 542
.201	.069 216 077	.251	.099 690 723	.301	.458 730 142	.351	.005 651 720
.202	.045 024 396	.252	.084 304 516	.302	.448 139 288	.352	1.997 954 892
.203	.021 075 081	.253	.069 043 011	.303	.437 620 780	.353	.990 303 664
.204	3.997 364 565	.254	.053 904 732	.304	.427 173 903	.354	.982 697 648
.205	.973 889 348	.255	.038 888 227	.305	.416 797 949	.355	.975 136 460
.206	.950 646 001	.256	.023 992 066	.306	.406 492 220	.356	.967 619 720
.207	.927 631 159	.257	.009 214 840	.307	.396 256 029	.357	.960 147 052
.208	.904 841 523	.258	2.994 555 163	.308	.386 088 605	.358	.952 718 087
.209	.882 273 855	.259	.980 011 672	.309	.375 989 547	.359	.945 332 455
.210	.859 924 981	.260	.965 583 022	.310	.365 957 923	.360	.937 989 795
.211	.837 791 786	.261	.951 267 891	.311	.355 993 170	.361	.930 689 746
.212	.815 871 215	.262	.937 064 976	.312	.346 094 642	.362	.923 431 955
.213	.794 160 269	.263	.922 972 994	.313	.336 261 701	.363	.916 216 070
.214	.772 656 005	.264	.908 990 681	.314	.326 493 720	.364	.909 041 744
.215	.751 355 536	.265	.895 116 792	.315	.316 790 077	.365	.901 908 633
.216	.730 256 027	.266	.881 350 103	.316	.307 150 159	.366	.894 816 397
.217	.709 354 697	.267	.867 689 406	.317	.297 573 357	.367	.887 764 700
.218	.688 648 815	.268	.854 133 512	.318	.288 059 083	.368	.880 753 211
.219	.668 135 699	.269	.840 681 248	.319	.278 606 738	.369	.873 781 600
.220	.647 812 718	.270	.827 331 461	.320	.269 215 741	.370	.866 849 542
.221	.627 677 286	.271	.814 083 013	.321	.259 885 517	.371	.859 956 716
.222	.607 726 886	.272	.800 934 783	.322	.250 615 498	.372	.853 102 802
.223	.587 958 965	.273	.787 885 669	.323	.241 405 122	.373	.846 287 488
.224	.568 371 136	.274	.774 934 581	.324	.232 253 835	.374	.839 510 450
.225	.548 960 972	.275	.762 080 448	.325	.223 161 088	.375	.832 771 410
.226	.529 726 114	.276	.749 322 213	.326	.214 126 342	.376	.826 070 035
.227	.510 664 239	.277	.736 658 834	.327	.205 149 061	.377	.819 406 032
.228	.491 773 069	.278	.724 089 286	.328	.196 228 719	.378	.812 779 102
.229	.473 050 365	.279	.711 612 556	.329	.187 364 793	.379	.806 188 952
.230	.454 493 924	.280	.699 227 648	.330	.178 556 768	.380	.799 635 287
.231	.436 101 585	.281	.686 933 578	.331	.169 804 136	.381	.793 117 821
.232	.417 871 221	.282	.674 729 378	.332	.161 106 394	.382	.786 636 265
.233	.399 800 745	.283	.662 614 091	.333	.152 463 046	.383	.780 190 338
.234	.381 888 102	.284	.650 586 777	.334	.143 873 596	.384	.773 779 758
.235	.364 131 275	.285	.638 646 506	.335	.135 337 571	.385	.767 404 250
.236	.346 528 275	.286	.626 792 363	.336	.126 854 482	.386	.761 063 538
.237	.329 077 165	.287	.615 023 449	.337	.118 423 857	.387	.754 757 351
.238	.311 776 013	.288	.603 338 862	.338	.110 045 230	.388	.748 485 421
.239	.294 622 938	.289	.591 737 735	.339	.101 718 139	.389	.742 247 481
.240	.277 616 088	.290	.580 219 199	.340	.093 442 126	.390	.736 043 268
.241	.260 753 636	.291	.568 782 399	.341	.085 216 740	.391	.729 872 522
.242	.244 033 792	.292	.557 426 493	.342	.077 041 534	.392	.723 734 985
.243	.227 454 785	.293	.546 150 651	.343	.068 916 069	.393	.717 630 401
.244	.211 014 895	.294	.534 954 053	.344	.060 839 907	.394	.711 558 518
.245	.194 712 401	.295	.523 835 890	.345	.052 812 618	.395	.705 519 087
.246	.178 545 630	.296	.512 795 365	.346	.044 833 777	.396	.699 511 858
.247	.162 512 929	.297	.501 831 691	.347	.036 902 963	.397	.693 536 588
.248	.146 612 675	.298	.490 944 003	.348	.029 019 759	.398	.687 593 034
.249	.130 843 267	.299	.480 131 804	.349	.021 183 754	.399	.681 680 956
.250	.115 203 132	.300	.469 394 069	.350	.013 394 542	.400	.675 800 115

TABLE III.

x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$
.400	1.675 800 115	.450	1.416 951 448	.500	1.213 061 319	.550	1.048 999 655
.401	.669 950 277	.451	.412 396 546	.501	.209 430 004	.551	.046 049 272
.402	.664 131 208	.452	.407 863 207	.502	.205 814 364	.552	.043 110 623
.403	.658 342 678	.453	.403 351 288	.503	.202 214 303	.553	.040 183 643
.404	.652 584 459	.454	.398 860 646	.504	.198 629 728	.554	.037 268 268
.405	.646 856 323	.455	.394 391 138	.505	.195 060 545	.555	.034 364 435
.406	.641 158 048	.456	.389 942 625	.506	.191 506 663	.556	.031 472 079
.407	.635 489 411	.457	.385 514 967	.507	.187 967 989	.557	.028 591 138
.408	.629 850 193	.458	.381 108 027	.508	.184 444 433	.558	.025 721 550
.409	.624 240 177	.459	.376 721 666	.509	.180 935 903	.559	.022 863 253
.410	.618 659 147	.460	.372 355 751	.510	.177 442 311	.560	.020 016 185
.411	.613 106 890	.461	.368 010 146	.511	.173 963 568	.561	.017 180 286
.412	.607 583 194	.462	.363 684 718	.512	.170 499 586	.562	.014 355 494
.413	.602 087 852	.463	.359 379 336	.513	.167 050 276	.563	.011 541 749
.414	.596 620 655	.464	.355 093 867	.514	.163 615 553	.564	.008 738 991
.415	.591 181 399	.465	.350 828 183	.515	.160 195 329	.565	.005 947 162
.416	.585 769 881	.466	.346 582 155	.516	.156 789 521	.566	.003 166 203
.417	.580 385 899	.467	.342 355 654	.517	.153 398 042	.567	.000 396 054
.418	.575 029 255	.468	.338 148 555	.518	.150 020 809	.568	0.997 636 657
.419	.569 699 750	.469	.333 960 732	.519	.146 657 738	.569	.994 887 956
.420	.564 397 190	.470	.329 792 060	.520	.143 308 746	.570	.992 149 892
.421	.559 121 381	.471	325 642 417	.521	.139 973 752	.571	.989 422 410
.422	.553 872 131	.472	.321 511 680	.522	.136 652 673	.572	.986 705 451
.423	.548 649 251	.473	.317 399 728	.523	.133 345 428	.573	.983 998 961
.424	.543 452 552	.474	.313 306 440	.524	.130 051 938	.574	.981 302 883
.425	.538 281 847	.475	.309 231 698	.525	.126 772 123	.575	.978 617 163
.426	.533 136 953	.476	.305 175 383	.526	.123 505 902	.576	.975 941 745
.427	.528 017 687	.477	.301 137 378	.527	.120 253 199	.577	.973 276 575
.428	.522 923 866	.478	.297 117 567	.528	.117 013 935	.578	.970 621 598
.429	.517 855 313	.479	.293 115 834	.529	.113 788 032	.579	.967 976 762
.430	.512 811 848	.480	.289 132 066	.530	.110 575 414	.580	.965 342 011
.431	.507 793 296	.481	.285 166 149	.531	.107 376 005	.581	.962 717 294
.432	.502 799 483	.482	.281 217 970	.532	.104 189 730	.582	.960 102 558
.433	.497 830 235	.483	.277 287 419	.533	.101 016 512	.583	.957 497 750
.434	.492 885 381	.484	.273 374 384	.534	.097 856 278	.584	.954 902 819
.435	.487 964 752	.485	.269 478 756	.535	.094 708 954	.585	.952 317 712
.436	.483 068 179	.486	.265 600 427	.536	.091 574 466	.586	.949 742 380
.437	.478 195 495	.487	.261 739 287	.537	.088 452 741	.587	.947 176 769
.438	.473 346 536	.488	.257 895 232	.538	.085 343 708	.588	.944 620 831
.439	.468 521 138	.489	.254 068 153	.539	.082 247 295	.589	.942 074 515
.440	.463 719 139	.490	.250 257 947	.540	.079 163 430	.590	.939 537 771
.441	.458 940 378	.491	.246 464 509	.541	.076 092 043	.591	.937 010 549
.442	.454 184 696	.492	.242 687 735	.542	.073 033 064	.592	.934 492 801
.443	.449 451 935	.493	.238 927 523	.543	.069 986 422	.593	.931 984 477
.444	.444 741 939	.494	.235 183 771	.544	.066 952 050	.594	.929 485 529
.445	.440 054 553	.495	.231 456 378	.545	.063 929 878	.595	.926 995 909
.446	.435 389 623	.496	.227 745 244	.546	.060 919 838	.596	.924 515 569
.447	.430 746 998	.497	.224 050 269	.547	.057 921 862	.597	.922 044 461
.448	.426 126 527	.498	.220 371 355	.548	.054 935 884	.598	.919 582 538
.449	.421 528 059	.499	.216 708 404	.549	.051 961 837	.599	.917 129 753
.450	.416 951 448	.500	.213 061 319	.550	.048 999 655	.600	.914 686 060

TABLE III.

x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$
.600	0.914 686 060	.650	0.803 147 349	.700	0.709 407 577	.750	0.629 822 070
.601	.912 251 412	.651	.801 112 123	.701	.707 687 542	.751	.628 354 757
.602	.909 825 764	.652	.799 083 940	.702	.705 973 114	.752	.626 891 973
.603	.907 409 069	.653	.797 062 766	.703	.704 264 268	.753	.625 433 701
.604	.905 001 282	.654	.795 048 570	.704	.702 560 980	.754	.623 979 921
.605	.902 602 358	.655	.793 041 317	.705	.700 863 226	.755	.622 530 616
.606	.900 212 253	.656	.791 040 976	.706	.699 170 981	.756	.621 085 766
.607	.897 830 921	.657	.789 047 514	.707	.697 484 222	.757	.619 645 354
.608	.895 458 319	.658	.787 060 899	.708	.695 802 923	.758	.618 209 361
.609	.893 094 403	.659	.785 081 099	.709	.694 127 063	.759	.616 777 770
.610	.890 739 130	.660	.783 108 083	.710	.692 456 616	.760	.615 350 562
.611	.888 392 455	.661	.781 141 818	711	.690 791 560	.761	.613 927 719
.612	.886 054 335	.662	.779 182 273	.712	.689 131 870	.762	.612 509 224
.613	.883 724 729	.663	.777 229 418	.713	.687 477 525	.763	.611 095 059
.614	.881 403 594	.664	.775 283 221	.714	.685 828 499	.764	.609 685 206
.615	.879 090 887	.665	.773 343 651	.715	.684 184 772	.765	.608 279 648
.616	.876 786 566	.666	.771 410 678	.716	.682 546 319	.766	.606 878 368
.617	.874 490 590	.667	.769 484 271	.717	.680 913 118	.767	.605 481 347
.618	.872 202 918	.668	.767 564 400	.718	.679 285 146	.768	.604 088 569
.619	.869 923 507	.669	.765 651 035	.719	.677 662 381	.769	.602 700 017
.620	.867 652 319	.670	.763 744 146	.720	.676 044 800	.770	.601 315 673
.621	.865 389 311	.671	.761 843 703	.721	.674 432 381	.771	.599 935 521
.622	.863 134 444	.672	.759 949 678	.722	.672 825 103	.772	.598 559 544
.623	.860 887 677	.673	.758 062 039	.723	.671 222 942	.773	.597 187 724
.624	.858 648 971	.674	.756 180 759	.724	.669 625 878	.774	.595 820 045
.625	.856 418 286	.675	.754 305 808	.725	.668 033 888	.775	.594 456 492
.626	.854 195 582	.676	.752 437 158	.726	.666 446 951	.776	.593 097 046
.627	.851 980 822	.677	.750 574 779	.727	.664 865 045	.777	.591 741 691
.628	.849 773 966	.678	.748 718 643	.728	.663 288 149	.778	.590 390 412
.629	.847 574 975	.679	.746 868 723	.729	.661 716 242	.779	.589 043 192
.630	.845 383 811	.680	.745 024 989	.730	.660 149 301	.780	.587 700 014
.631	.843 200 436	.681	.743 187 414	.731	.658 587 308	.781	.586 360 864
.632	.841 024 813	.682	.741 355 969	.732	.657 030 239	.782	.585 025 723
.633	.838 856 903	.683	.739 530 628	.733	.655 478 076	.783	.583 694 577
.634	.836 696 670	.684	.737 711 362	.734	.653 930 796	.784	.582 367 410
.635	.834 544 076	.685	.735 898 145	.735	.652 388 380	.785	.581 044 206
.636	.832 399 084	.686	.734 090 949	.736	.650 850 806	.786	.579 724 949
.637	.830 261 659	.687	.732 289 748	.737	.649 318 055	.787	.578 409 624
.638	.828 131 762	.688	.730 494 513	.738	.647 790 106	.788	.577 098 215
.639	.826 009 359	.689	.728 705 219	.739	.646 266 939	.789	.575 790 706
.640	.823 894 413	.690	.726 921 839	.740	.644 748 534	.790	.574 487 083
.641	.821 786 888	.691	.725 144 347	.741	.643 234 872	.791	.573 187 329
.642	.819 686 749	.692	.723 372 716	.742	.641 725 932	.792	.571 891 430
.643	.817 593 961	.693	.721 606 920	.743	.640 221 694	.793	.570 599 371
.644	.815 508 489	.694	.719 846 934	.744	.638 722 139	.794	.569 311 136
.645	.813 430 298	.695	.718 092 731	.745	.637 227 248	.795	.568 026 711
.646	.811 359 353	.696	.716 344 296	.746	.635 737 001	.796	.566 746 080
.647	.809 295 619	.697	.714 601 573	.747	.634 251 379	.797	.565 469 228
.648	.807 239 063	.698	.712 864 568	.748	.632 770 363	.798	.564 196 142
.649	.805 189 651	.699	.711 133 244	.749	.631 293 933	.799	.562 926 806
.650	.803 147 349	.700	.709 407 577	.750	.629 822 070	.800	.561 661 205

TABLE III.

x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$
.800	0.561 661 205	.850	0.502 841 096	.900	0.451 744 066	.950	0.407 095 814
.801	.560 399 326	.851	.501 748 215	.901	.450 791 668	.951	.406 261 278
.802	.559 141 152	.852	.500 658 399	.902	.449 841 833	.952	.405 428 902
.803	.557 886 671	.853	.499 571 640	.903	.448 894 550	.953	.404 598 677
.804	.556 635 868	.854	.498 487 924	.904	.447 949 811	.954	.403 770 597
.805	.555 388 729	.855	.497 407 241	.905	.447 007 608	.955	.402 944 654
.806	.554 145 238	.856	.496 329 580	.906	.446 067 931	.956	.402 120 842
.807	.552 905 383	.857	.495 254 930	.907	.445 130 772	.957	.401 299 153
.808	.551 669 149	.858	.494 183 279	.908	.444 196 121	.958	.400 479 580
.809	.550 436 523	.859	.493 114 617	.909	.443 263 971	.959	.399 662 117
.810	.549 207 489	.860	.492 048 933	.910	.442 334 314	.960	.398 846 756
.811	.547 982 035	.861	.490 986 216	.911	.441 407 136	.961	.398 033 491
.812	.546 760 147	.862	.489 926 455	.912	.440 482 434	.962	.397 222 313
.813	.545 541 810	.863	.488 869 639	.913	.439 560 198	.963	.396 413 218
.814	.544 327 012	.864	.487 815 758	.914	.438 640 419	.964	.395 606 197
.815	.543 115 739	.865	.486 764 801	.915	.437 723 089	.965	.394 801 243
.816	.541 907 977	.866	.485 716 757	.916	.436 808 198	.966	.393 998 351
.817	.540 703 713	.867	.484 671 616	.917	.435 895 740	.967	.393 197 513
.818	.539 502 933	.868	.483 629 367	.918	.434 985 705	.968	.392 398 722
.819	.538 305 624	.869	.482 590 000	.919	.434 078 084	.969	.391 601 972
.820	.537 111 774	.870	.481 553 505	.920	.433 172 871	.970	.390 807 256
.821	.535 921 368	.871	.480 519 870	.921	.432 270 056	.971	.390 014 567
.822	.534 734 394	.872	.479 489 087	.922	.431 369 631	.972	.389 223 899
.823	.533 550 838	.873	.478 461 143	.923	.430 471 588	.973	.388 435 245
.824	.532 370 688	.874	.477 436 030	.924	.429 575 919	.974	.387 648 598
.825	.531 193 930	.875	.476 413 737	.925	.428 682 615	.975	.386 863 952
.826	.530 020 553	.876	.475 394 253	.926	.427 791 669	.976	.386 081 301
.827	.528 850 542	.877	.474 377 570	.927	.426 903 073	.977	.385 300 637
.828	.527 683 886	.878	.473 363 676	.928	.426 016 818	.978	.384 521 955
.829	.526 520 571	.879	.472 352 562	.929	.425 132 897	.979	.383 745 248
.830	.525 360 586	.880	.471 344 218	.930	.424 251 301	.980	.382 970 509
.831	.524 203 917	.881	.470 338 633	.931	.423 372 023	.981	.382 197 732
.832	.523 050 552	.882	.469 335 799	.932	.422 495 055	.982	.381 426 911
.833	.521 900 479	.883	.468 335 705	.933	.421 620 389	.983	.380 658 039
.834	.520 753 685	.884	.467 338 341	.934	.420 748 017	.984	.379 891 111
.835	.519 610 157	.885	.466 343 699	.935	.419 877 931	.985	.379 126 119
.836	.518 469 885	.886	.465 351 767	.936	.419 010 124	.986	.378 363 057
.837	.517 332 855	.887	.464 362 536	.937	.418 144 587	.987	.377 601 920
.838	.516 199 055	.888	.463 375 998	.938	.417 281 314	.988	.376 842 700
.839	.515 068 474	.889	.462 392 142	.939	.416 420 297	.989	.376 085 393
.840	.513 941 099	.890	.461 410 958	.940	.415 561 527	.990	.375 329 991
.841	.512 816 919	.891	.460 432 438	.941	.414 704 998	.991	.374 576 488
.842	.511 695 921	.892	.459 456 572	.942	.413 850 701	.992	.373 824 879
.843	.510 578 093	.893	.458 483 350	.943	.412 998 630	.993	.373 075 157
.844	.509 463 425	.894	.457 512 764	.944	.412 148 776	.994	.372 327 317
.845	.508 351 903	.895	.456 544 803	.945	.411 301 133	.995	.371 581 351
.846	.507 243 517	.896	.455 579 459	.946	.410 455 693	.996	.370 837 255
.847	.506 138 255	.897	.454 616 723	.947	.409 612 448	.997	.370 095 022
.848	.505 036 105	.898	.453 656 584	.948	.408 771 392	.998	.369 354 646
.849	.503 937 056	.899	.452 699 035	.949	.407 932 516	.999	.368 616 121
.850	.502 841 096	.900	451 744 066	.950	.407 095 814	1.000	.367 879 441

TABLE IV.

x	$\frac{e^{-x}}{x}$	x	$\frac{e^{-x}}{x}$
1.00	0.367 879 441	1.50	0.148 753 440
1.01	.360 612 851	1.51	.146 297 999
1.02	.353 524 451	1.52	.143 889 399
1.03	.346 608 700	1.53	.141 526 580
1.04	.339 860 271	1.54	.139 208 507
1.05	.333 274 047	1.55	.136 934 177
1.06	.326 845 104	1.56	.134 702 610
1.07	.320 568 708	1.57	.132 512 855
1.08	.314 440 302	1.58	.130 363 986
1.09	.308 455 499	1.59	.128 255 102
1.10	.302 610 076	1.60	.126 185 324
1.11	.296 899 965	1.61	.124 153 798
1.12	.291 321 245	1.62	.122 159 691
1.13	.285 870 138	1.63	.120 202 193
1.14	.280 543 002	1.64	.118 280 514
1.15	.275 336 321	1.65	.116 393 884
1.16	.270 246 708	1.66	.114 541 554
1.17	.265 270 890	1.67	.112 722 794
1.18	.260 405 711	1.68	.110 936 890
1.19	.255 648 121	1.69	.109 183 150
1.20	.250 995 177	1.70	.107 460 897
1.21	.246 444 033	1.71	.105 769 469
1.22	.241 991 940	1.72	.104 108 225
1.23	.237 636 242	1.73	.102 476 538
1.24	.233 374 369	1.74	.100 873 793
1.25	.229 203 837	1.75	.099 299 396
1.26	.225 122 243	1.76	.097 752 764
1.27	.221 127 261	1.77	.096 233 327
1.28	.217 216 641	1.78	.094 740 532
1.29	.213 388 204	1.79	.093 273 838
1.30	.209 639 841	1.80	.091 832 716
1.31	.205 969 509	1.81	.090 416 650
1.32	.202 375 229	1.82	.089 025 138
1.33	.198 855 064	1.83	.087 657 687
1.34	.195 407 215	1.84	.086 313 819
1.35	.192 029 823	1.85	.084 993 063
1.36	.188 721 160	1.86	.083 694 963
1.37	.185 479 533	1.87	.082 419 070
1.38	.182 303 299	1.88	.081 164 950
1.39	.179 190 867	1.89	.079 932 174
1.40	.176 140 689	1.90	.078 720 326
1.41	.173 151 265	1.91	.077 528 998
1.42	.170 221 139	1.92	.076 357 793
1.43	.167 348 897	1.93	.075 206 320
1.44	.164 533 166	1.94	.074 074 201
1.45	.161 772 612	1.95	.072 961 062
1.46	.159 065 942	1.96	.071 866 541
1.47	.156 411 895	1.97	.070 790 282
1.48	.153 809 249	1.98	.069 731 938
1.49	.151 256 816	1.99	.068 691 169
1.50	.148 753 440	2.00	.067 667 642

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 44. A REACTION WHOSE RATE IS DIMINISHED BY RAISING THE TEMPERATURE

BY CLARA C. BENSON

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. 8, 1904)

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Reprinted from the Journal of Physical Chemistry, Vol. 8, No. 2. February, 1904.

A REACTION WHOSE RATE IS DIMINISHED BY RAISING THE TEMPERATURE

BY CLARA C. BENSON

Towards the close of my measurements of the rates of the reactions in solutions containing chromic acid, potassium iodide and ferrous sulphate,[1] I was surprised to find that the amount of iodine liberated in a minute at 30° was less than that set free in the same time at 0° (see Table 24).

Taken by itself, this result does not prove that the rate of liberation of iodine is less at 30° than at 0°, and at first I thought it most likely that at the higher temperature the reaction was over before the minute was up. Analyses at the expiration of two, four and eight minutes, however, showed that, far from being completed within sixty seconds, the reaction was still proceeding after four minutes; and as in blank experiments (no $FeSO_4$) no iodine was set free inside of eight minutes, the conclusion is unavoidable that the oxidation of potassium iodide by chromic acid in presence of ferrous sulphate is retarded by raising the temperature.

The measurements detailed in the following tables show that the nature of the reaction at 30° is much the same as at 0°. At the higher temperature, as at the lower, the rate is proportional to the first power of the concentration of the iodide (Tables 24 and 25), to the first power of the concentration of the ferrous salt (Tables 24 and 26) and to the 1.7th power of the concentration of the bichromate (Tables 24 and 27). The retarding influence of the products of oxidation (Tables 24, 28, 34 and 30) is somewhat less at the higher temperature, and its "ageing" (Tables 15 and 29) is more rapid. In experiments carried out without addition of the products of oxidation, the rate is proportional to the fourth power of the concentration of the acid (Tables 31 and 32);

[1] Jour. Phys. Chem. 7, 356 (1903).

while in their presence it varies with the second or third power only (Tables 24, 33 and 34). At zero, in the presence of excess of the products of oxidation the rate is proportional to the fourth power, while in the absence of ferric salts the reaction is too quick for accurate measurement. It is a consequence of this difference in the order of the reaction with respect to the acid, that while in Tables 24, 25, 26 and 27 the reaction is four or five times as quick at 0° as at 30.2°, in Tables 33 and 34 where larger quantities of the acid were employed, it is seven and fifteen times as quick, respectively.

A single experiment (Table 35) shows that, as was to be expected, the rate of oxidation of ferrous sulphate by chromic acid in absence of potassium iodide is accelerated by heat; Mr. DeLury[1] has found that the same is true for the oxidation of potassium iodide in absence of ferrous salts.

The only reactions hitherto studied whose rates have a negative temperature coefficient, so far as I am aware, are those in which a colloidal catalytic agent is involved; in these cases the rate passes through a maximum as the temperature is increased, and then falls off because of the coagulation of the colloid. In the experiments of the present paper the only colloid present is the ferric salt, and its coagulation, instead of retarding, accelerates the reaction.

It seems probable, however, that as the rates in other complex systems came to be studied, further cases of negative temperature coefficients will be met with, and that the present instance may be regarded as typical of a new class. Both ferroiodion theory and peroxide theory are ready with an explanation of the retardation; the former by assuming that the amount of $\overset{+}{Fe}I$ undissociated is less at high temperatures, and the latter by asserting that as the temperature is raised the peroxide reacts more with the residual ferrous salt, and less with the iodide.

I regret that in the time at my disposal I am not able to undertake the large amount of work necessary to ascertain whether either theory could be brought into accord with quan-

[1] Jour. Phys. Chem. 7, 239 (1903).

titative measurements; and at the close of this research I wish to express my sincere thanks to Prof. W. Lash Miller for his interest and assistance.

The University of Toronto,
November, 1903.

The experiments were carried out as described in this Journal, **7**, 357, and the abbreviations made use of in these tables are those explained in that paper.

Ac, 10 represents ten cc of 0.059*F* sulphuric acid (0.059 gram-formula-weights H_2SO_4 per liter); *Cr*, 10, ten cc of 0.0083*F* $K_2Cr_2O_7$ (including unreduced bichromate in the "*Ox*"); *KI*, 10, ten cc of 0.0479*F KI*; *Fe*, 1.0, one cc of 0.05*F* ferrous sulphate; *Ox*, 5, the product of oxidation of five cc of 0.05*F* ferrous sulphate: θ is the duration of the reaction in minutes; *As*, the number of cc of *n*/100 sodium arsenite equivalent to the iodine liberated; *V*, the total volume in cc of the reacting mixture.

For the sake of convenience, the tables are numbered consecutively with those of the previous paper, "As, 0° (Table 3)," for example, referring to Table 3, Jour. Phys. Chem. **7**, 379.

I take this opportunity of correcting the following misprints: Table 22 (Jour. Phys. Chem. **7**, 387), second column, should read: 100, 129, 152, 162, in place of 100, 116, 126, 131. In equation 7 (p. 372) the sign of equality has been omitted after $dy/d\theta$, and on page 376 the / sign has been omitted from the expression $a^2/k(1-a) = 1077$.

TABLE 24

Ac, 10; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700

θ	0.5	1	2	4	8
As, 30.2° (Expt. 37)	—	0.55	1.05	1.80	2.40
As, 0° (Table 3)	1.05	1.90	3.10	4.30	5.60

Blanks (30.2°): $\theta = 4$, As = 0; $\theta = 8$, As = 0.45

TABLE 25

Ac, 10; Cr, 20; KI, 10; Ox, 5; Fe, 1.0; V, 700

θ	1	2	4	8
As, 30.2° (Expt. 38)	—	0.80	1.10	1.85
As 0° (Table 8)	1.40	2.20	3.30	4.30

Blank (30.2°): $\theta = 8$; As = 0

TABLE 26

Ac, 10; Cr, 20; KI, 20; Ox, 5; Fe, 0.5; V, 700

θ	1	2	4	8
As, 30.2° (Expt. 39)	—	0.55	0.90	1.45
As, 0° (Table 3)	1.00	1.75	2.50	3.30

Blanks (30.2°): $\theta = 4$, As = 0; $\theta = 8$, As = 0.45

TABLE 27

Ac, 10; Cr, 30; KI, 20; Ox, 5; Fe, 1.0; V, 700

θ	0.5	1	2	4	8
As, 30.2° (Expt. 40)	—	0.80	1.45	2.30	2.80
As, 0° (Table 6)	1.75	2.95	4.15	5.30	—

Blanks (30.2°): $\theta = 5$, As = 0; $\theta = 8$; As = 0.60

TABLE 28

Ac, 10; Cr, 20; KI, 20; Ox, 0; Fe, 1.0; V, 700

θ	0.5	1	2	4	8
As, 30.2° (Expt. 41)	0.90	1.45	1.80	2.30	2.60
As, 0° (Table 12)	3.95	5.00	5.85	6.30	—

Blank (30.2°): $\theta = 8$, As = 0

TABLE 29

Expt. 42. Ac, 10; Cr, 20; KI, 10; Ox, 5; Fe, 1.0; V, 700; Temp. 30.2° C

Age of Ox	fresh	fresh	3 days	3 days
θ	2	4	2	4
As	0.80	1.10	1.10	1.35

TABLE 30

Expt. 43. Ac, 20; Cr, 20; KI, 20; Ox, 0; Fe, 1.0; V, 700; Temp. 30.2° C

θ	0.25	0.5	1.0
As	2.65	3.40	4.40

TABLE 31

Expt. 44. Ac, 10; Cr, 10; KI, 20; Ox, 0; Fe, 1.0; V, 700; Temp. 39.7° C

θ	2	4	8	16
As	0.30	1.10	1.35	2.25

TABLE 32

Expt. 45. Ac, 20; Cr, 10; KI, 20; Ox, 0; Fe, 1.0; V, 700; Temp. 39.7° C

θ	0.5	1	2
As	1.40	2.15	2.70

TABLE 33

Ac, 15; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700

θ	0.5	1	2
As, 30.2° (Expt. 46)	0.55	1.15	2.00
As, 0° (Table 5)	3.00	4.60	6.00

TABLE 34

Ac, 20; Cr, 20; KI, 20; Ox, 5; Fe, 1.0; V, 700.

θ	0.25	0.5	1	2	4
As, 30.2° (Expt. 47)	—	1.35	2.25	3.40	4.30
As, 0° (Table 5)	4.05	5.75	7.15	8.00	—

Blank (30.2°): $\theta = 4$, As = 0

TABLE 35 (Expt. 48)

In the mixture Ac = 20, Cr = 10, Ox = 5, Fe = 1.0, V = 700, at 0°, after half a minute, 0.78 cc of the ferrous salt remained unoxidized (Table 19).

In the same mixture at 30.2°, the amount of ferrous sulphate remaining after half a minute caused the liberation (in four minutes) of iodine equivalent to As = 1.15, when KI = 20 was added, and water enough to bring the total volume up to 800 cc.

But in the mixture Ac = 20, Cr = 10, KI = 20, Ox = 5, Fe = 0.75, V = 800, for $\theta = 4$, As = 1.70. Consequently, *less* than 0.75 cc of $FeSO_4$ must have remained unoxidized after half a minute in the previous experiment (See Jour. Phys. Chem. **7**, 1 (1903)).

List of Experiments

Expt.	Table	Ac	Cr	KI	Ox	Fe	Temp.	Page	
1	1	10	10	20	5	1	0°	378	See also Tables 16, 17
2	1	10	10	20	5	0.5	0	378	" " " 17
3	2	15	10	20	5	1	0	378	
4	2	15	10	20	5	0.5	0	378	
5	3	10	20	20	5	1	0	379	" " " 16, 17
6	3	10	20	20	5	0.5	0	379	" " " 17
7	4	20	10	20	5	1	0	379	
8	4	20	10	20	5	0.5	0	379	
9	5	20	20	20	5	1	0	380	" " " 16, 17
10	5	15	30	20	5	1	0	380	
11	5	15	20	20	5	1	0	380	
12	6	10	30	20	5	1	0	380	
13	6	10	30	20	5	0.5	0	380	
14	7	10	20	5	5	1	0	381	" " " 16, 17
15	7	10	20	5	5	0.5	0	381	" " " 17
16	8	10	20	10	5	1	0	381	" " " 16, 17
17	8	10	20	10	5	0.5	0	381	" " " 17
18	9	10	20	30	5	1	0	382	
19	9	10	20	30	5	0.5	0	382	
20	10	10	20	20	5	2	0	382	
21	10	10	20	20	5	1.5	0	382	
22	10	20	10	20	5	0.25	0	382	
23	12	10	20	20	0	1	0	383	" " " 16, 17
24	12	10	20	20	2.5	1	0	383	
25	12	10	20	20	3.3	1	0	383	
26	12	10	20	20	5.0	1	0	383	
27	12	10	20	20	10	1	0	383	
28	13	10	20	20	0	1	0	384	K_2SO_4 added
29	13	10	20	20	0	1	0	384	$Cr_2(SO_4)_3$ added
30	13	10	20	20	5	1	0	384	Iodine added
31	13	20	10	20	5	0	0	384	Haemoglobin added
32	13	10	20	20	0	0	0	384	Ferrosomatose added
33	13	10	20	20	0	0	0	384	$K_4Fe(CN)_6$ added
—	15	10	20	20	age	1	0	384	
34	19	10	10	0	5	1	0	386	
35	19	10	20	0	5	1	0	386	See also Table 17
36	19	20	10	0	5	1	0	386	
37	24	10	20	20	5	1	30.2	118	
38	25	10	20	10	5	1	30.2	119	
39	26	10	20	20	5	0.5	30.2	119	
40	27	10	30	20	5	1	30.2	119	
41	28	10	20	20	0	1	30.2	119	
42	29	10	20	10	age	1	30.2	119	
43	30	20	20	20	0	1	30.2	119	
44	31	10	10	20	0	1	39.7	120	
45	32	20	10	20	0	1	39.7	120	
46	33	15	20	20	5	1	30.2	120	
47	34	20	20	20	5	1	30 2	120	
48	35	20	10	20	5	0.75	30.2	120	

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 45: ON THE DECOMPOSITION OF BENZENE AT HIGH TEMPERATURES

BY G. W. MORE

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ON THE DECOMPOSITION OF BENZENE AT HIGH TEMPERATURES.

BY G. W. McKEE.

In the manufacture of both coal gas and carburetted water-gas it is a matter of great practical importance that we should have a knowledge of the temperatures at which the various hydrocarbons decompose (especially those used for enriching purposes), and the extent to which the decomposition increases with increasing temperature. The most important among these reactions is the decomposition of benzene (C_6H_6). Suppose, for instance, we start with the gas oils which are higher normal paraffins, the pyrogenetic reactions are such as are indicated by the following: — Higher paraffins → lower paraffins → olefines → acetylenes → benzenes → diphenyl, &c. → naphthalene, &c. → tarry matter → carbon and hydrogen. The great value of benzene in increasing the illuminating value of gas is well known; and the nuisance that arises from the formation of solid substances like diphenyl and naphthalene, which stop up both pipes and machinery, is one of the greatest obstacles in the manufacture of coal gas.

The precise nature of the above reactions becomes then of practical importance, and the experiments carried out were undertaken to throw some light, if possible, on the transition temperatures of these substances. The apparatus used is shown in Fig. 1.

To heat the furnace F, the rheostat R and the furnace F were joined in parallel and connected with the street circuit. The switch S was also inserted to permit of complete control of the current from the working table. The furnace was heated by means of hot platinum resistance wires embedded in its fire-brick walls It was found con-

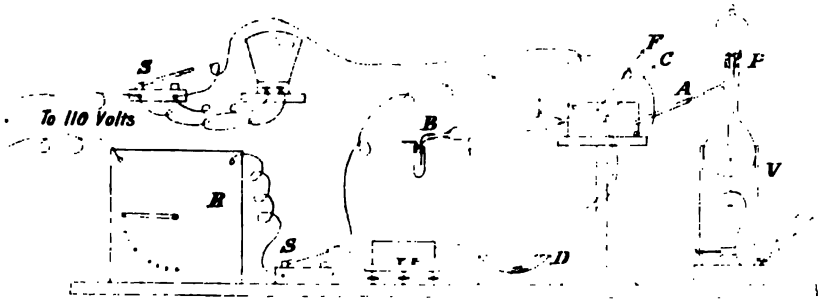

FIG. 1.

venient to surround it with $\frac{3}{4}$ in. asbestos millboard, pieces of which were readily cut without disturbing the edges, by placing it between pine boards and using a saw. In assembling these into a box the edges were preserved for nailing by securing the pieces in a vice. In front of the furnace was placed a piece of asbestos with three holes, which were punched by means of a sharpened brass tube against a hardwood block. Two of these were for the inlet and outlet of the copper tube which was to carry the benzol vapour, while the third was for the introduction of a thermo couple.

The pyrometer used was a Le Chatelier made by Keiser and Schmidt, Berlin. A thermo-couple, of 50 cm. length, of platinum and platinum with 10 per cent. rhodium, was introduced into the furnace by means of a porcelain tube about $\frac{3}{8}$ in. in diameter and perforated by two holes, each about 1 mm. in diameter. To the thermo-couple were joined the copper wires in the porcelain dish D, which was kept at zero by means of melting ice. The copper wires were joined, as shown, to the pyrometer, which was provided with an auxiliary switch. The calibrations of the thermo-couple were plotted on section paper for interpolation purposes.

For vaporising the benzene the device shown at V in the right of the figure was used. An electric lamp was mounted on a block. On the same block was secured a piece of tin pipe about 4 ins. in diameter. A piece of $\frac{1}{4}$ in. asbestos was cut and rolled to fit the inside of the tin and thus prevent loss of heat by radiation. The benzene to be decomposed was placed in the pear-shaped funnel P. The stem of this funnel was so drawn out that the drops issuing from it would be very small; the supply was further capable of control by the tap on the stem of the funnel. In this way small drops of benzene were allowed to fall on the heated bottom of the flask, where they were at once vaporised and subsequently passed through the furnace, the rate being easily regulated by counting the drops.

About 6 ft. of seamless copper tubing, thin-walled, and about $\frac{1}{4}$ in. external diameter, the temper drawn by passing it slowly through a blow-pipe flame, were coiled around a prepared spool, so that a coil of about $4\frac{1}{2}$ ft. of it fitted nicely in the furnace, leaving an aperture between the coils sufficiently large to allow the tube which insulated the thermo-couple being passed through to the middle of the furnace. The ends of the copper tube passed through the holes shown in the asbestos pad which formed the door of the furnace, and were bent at right angles so as to terminate at A and B (see Fig. 1).

The distilling flask was selected so that its delivery tube fitted accurately into the copper tube at A, and the joint was further secured by means of suitable packing. The

other end B, of the copper tube was provided with a short glass condenser 6 ins. in length, while an adapter of glass tubing was slipped over the end of the copper tube, and secured by means of a section of rubber tubing. The adapter passed through a stopper into a small glass vessel in which were caught the products of decomposition.

To determine whether the benzene had been decomposed or not, specific gravity determinations were made by means of a pyknometer. In all cases these were taken at 18° C., the variation of the specific gravity of benzene for a difference of one degree centigrade being very considerable.

	Per Cent.
Specific gravity of the benzol employed	0·88181
„ of products after heating to 448° C.	0·88175
„ „ „ 550° C.	0·88203
„ „ „ 664° C.	0·88362
„ „ „ 720° C.	0·88963
„ „ „ 765° C.	0·90276

These results may be expressed graphically by the following curve :—

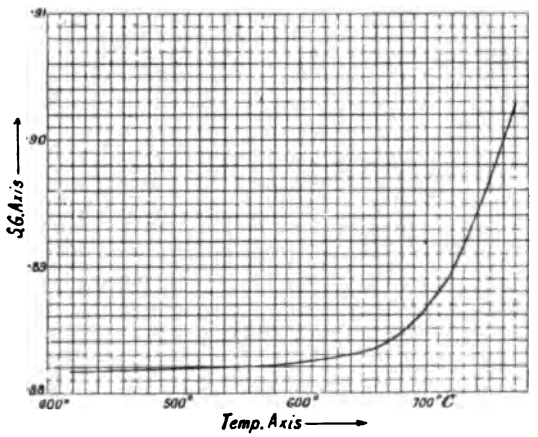

FIG. 2.

A second method of determining if decomposition had taken place was to slowly evaporate a portion of the product to dryness, and to examine the residue, if any, by the polarising microscope. The accompanying table shows the results obtained. The tube was further washed thoroughly with pure benzol, and a number of fractions taken from 544° to 550°, but it could not be said that the action became decidedly perceptible until after 550° had been passed. From that point onwards reference to the

curve (Fig. 2) shows the extent to which the benzene vapours become decomposed as the temperature rises.

Quantity evaporated.	Temperature to which it had been subjected in passing through Tube.	Appearance when examined by Polarising Microscope.
c.c.	° C.	
20	Not heated	No crystalline structure.
10	494	" "
10	526	" "
5	550	Polarisation colours scarcely visible in residue.
5	562	Crystalline residue prominent, small crystals easily distinguished.

It would thus seem advisable, in adding enriching material to, say, a water-gas, to prevent the added material from being subjected to a temperature much greater than 700° C.

The author wishes to express his thanks to Prof. W. R. Lang, of the University of Toronto, for the interest shown and the assistance rendered in this investigation.

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NOTE ON THE ACTION OF METHYLAMINE ON CHROMIC CHLORIDE, BY W. R. LANG AND E. H. JOLLIFFE

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THE ACTION OF LIQUEFIED AMMONIA ON CHROMIC CHLORIDE.

By W. R. Lang and C. M. Carson.

Received January 30, 1904.

Jörgensen describes a number of compounds derived from chromic chloride by the action on chromous chloride of aqueous ammonia, ammonium chloride and subsequent oxidation.

The authors have obtained similar substances by the direct action of dry liquid ammonia on violet chromic chloride at low temperatures. Violet chromic chloride is not acted upon by aqueous ammonia nor by dry ammonia gas, but liquid ammonia acts upon it readily, completely transforming it into a salmon-colored powder.

Experimental.—Three grams of powdered chromic chloride were placed in a vessel made of combustion tubing, closed at the lower end and drawn out at the neck to allow of the tube being sealed at the blowpipe. The whole was placed in a freezing-mixture, consisting of solid carbonic acid and ether, and ammonia, dried over potassium hydroxide, was passed in. No action took place until liquefaction began, when the chromic chloride swelled up and became pasty, the color changing at the same time to a dark salmon-pink. Ammonia in considerable excess was allowed to accumulate on the top of the mass and the tube was then sealed. The tube containing the salmon-colored material was set aside for a week at the room temperature, being shaken occasionallly to insure thorough mixing. Subsequent experiments showed the action of the ammonia to have been complete from the first, so in preparing further quantities this was omitted. The liquid ammonia on standing separated out colorless. The tube was then cooled to —35° and opened, the temperature raised gradually to 0°, at which it was kept constant for twenty-four hours, and the dry powder remaining kept for investigation. Further quantities were prepared in the same way and left standing at 0° for two and four days respectively. Another portion of the powder was left at 15° C. for two days, and yet another portion was heated to 110° C. for the same length of time when the color became more distinctly pink. Analyses of the powder obtained at 0°, 15°, and 110° respectively yielded:

	(A) At 0°. Per cent.	(B) At 15°. Per cent.	(C)[1] At 110°. Per cent.
Chromium	20.1	20.6	21.7
Chlorine	41.1	41.6	44.1
Ammonia	38.6	37.8	34.1
	99.8	100.0	99.9
Corresponding to molecules of NH_3 per molecule of Cr_2Cl_6	11.7	11.2	9.7

[1] This analysis was done by Mr. J. A. M. Dawson.

Further heating continued for twenty-four hours to 130° brought about the separation of a small amount of chromic oxide but complete decomposition into chromic oxide did not take place until a temperature of 180° was reached.

From the analytical results it was evident that the powders contained a mixture of substances, and the following investigation led to the isolation of two definite compounds therefrom.

I. The powder which had remained at 0° was treated with a small quantity of cold water, 5 cc. to every gram of the substance. Partial solution took place, and on filtering off from the undissolved solid, a clear solution of a brown color was obtained, which on standing in the air for even a short time, evolved ammonia and deposited chromium hydroxide. On removing the precipitated chromium hydroxide and rapidly evaporating *in vacuo*, yellow crystals separated out, which were collected and dried between filter-paper (for convenience let α indicate the yellow crystals). The residue from this first extraction with water was treated in the cold with a further quantity of the solvent and filtered. Evaporation *in vacuo* yielded, when carefully conducted, red crystals (β). When the concentration in the vacuum desiccator was conducted too slowly, slight decomposition into gelatinous chromium hydroxide took place with the evolution of ammonia, but if rapidly conducted in shallow evaporating dishes, the crystals separated readily from the solution and no ammonia was evolved. Analysis of the yellow compound and the red compound gave:

	α-Salt. Per cent.	β-Salt. Per cent.
Chromium	18.7	21.52
Chlorine	38.0	43.20
Ammonia	36.6	35.00
Water (by difference)	6.7	0.00
	100.00	99.72

The composition of the yellow α-compound thus corresponds with the formula $Cr_2Cl_6,12NH_3,2H_2O$, and that of the red β-compound with $Cr_2Cl_6,10NH_3$.

II. The powder obtained by keeping the original substance at 15° was similarly extracted with water, and from it were obtained yellow and red crystals, whose composition and properties were identical with the α- and β-compounds obtained in I.

III. Treatment of the original pink substance with cold water,

which had been maintained for two days at 100° C., yielded no α-crystals, but the red β-compound only.

PROPERTIES OF THE α-AND β-CRYSTALS.

The yellow crystals are soluble in water, but insoluble in hydrochloric acid and in alcohol. From the aqueous solution all the chlorine is precipitated in the cold by silver nitrate. On standing at 110° for two days, the yellow crystals are changed partly into a red powder, with separation of chromic oxide. These crystals evidently correspond with the *luteochromium* compounds obtained by Jörgensen[1] of the general formula $Cr_2 12NH_3X_6$.

The red compound crystallizes in small perfectly formed cubes and octahedra. They dissolve in cold water slowly, while hot water causes a separation of chromium hydroxide. Hydrochloric acid and alcohol exert no solvent action on them. Further, when the crystals are treated with liquid ammonia, no change takes place, and on addition of a small quantity of violet chromium chloride to the mixture of the salt and ammonia the chromic chloride reacts at once with the ammonia, yielding a pink powder from which the β-crystals may be separated mechanically. On treating the mixed crystals and powder with cold water, the latter readily dissolved away, leaving the red crystals untouched. The composition of this β-compound, $Cr_2 10NH_3Cl_6$, points to its being *chlorpurpureochromium chloride.*

CHEMICAL LABORATORY, UNIVERSITY OF TORONTO.

NOTE ON THE ACTION OF METHYLAMINE ON CHROMIC CHLORIDE.

BY W. R. LANG AND R. H. JOLLIFFE.

Received January 30, 1904.

A SOLUTION of methylamine was gently heated and the gas conducted through drying towers filled with potassium hydroxide to a glass tube containing chromium chloride and immersed in a freezing-mixture at a temperature of —10°. As soon as the liquid methylamine collected in the tube, combination between it and the chromic chloride took place and a substance of a pale pink color, closely resembling the ammonia compound (Lang and Carson), was formed. The excess of methylamine was allowed to pass off

[1] *J. prakt. Chem.*, [2] 30, 1.

and the contents of the tube dissolved in water. The substance was very soluble and the least possible quantity of water was used. The solution, on rapid evaporation *in vacuo*, yielded dark red crystals. Considerable difficulty was experienced in obtaining these crystals, owing to the rapidity with which the solution decomposed into chromic hydroxide; consequently the analysis of the crystals obtained by repeated operations had to be made on very small quantities. Analysis of the crystals thus obtained from the compound at a temperature of 15° gave:

	Found. Per cent.	Calculated for $Cr_2Cl_6.10CH_3NH_2$. Per cent.
Chromium	16.25	16.68
Chlorine	35.20	33.92
Methylamine	48.50	49.6
	99.95	100.00

Crystals produced in a similar manner from the original compound, previously heated to 94°, gave:

	Found. Per cent.	Calculated. Per cent.
Chromium	16.55	16.61
Chlorine	34.19	33.86
Methylamine	48.89	49.53
	99.63	100.00

The composition of these crystals is therefore $Cr_2Cl_6.10CH_3NH_2$, corresponding to the similarly constituted chloropurpureochromium chloride obtained (Lang and Carson) from anhydrous ammonia and chromic chloride.

On heating to 100° the compound formed by the direct action of methylamine on chromic chloride, analysis showed it to contain 43.26 per cent. of methylamine, which would point to its composition being Cr_2Cl_6, $8CH_3NH_2$, the percentage in this latter being 43.8. At 124° C. complete decomposition into Cr_2O_3 took place.

The analogy between the crystals thus obtained and the chloropurpureo compound is evident. The great difficulty of obtaining pure methylamine on the American continent prevented the investigation of these substances being continued further or more accurate analyses being made. Aniline and methylaniline had no action on the violet chromic chloride whether in the cold or when heated together. The effect of heating for any length of time in a sealed tube was not tried.

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No. 17. A MECHANICAL MODEL TO ILLUSTRATE THE GAS LAWS, BY FRANK B. KENRICK

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A MECHANICAL MODEL TO ILLUSTRATE THE GAS LAWS

BY FRANK B. KENRICK

The difficulty of getting elementary students to grasp the fundamental ideas of the gas laws, Carnot's cycle, the entropy function, etc., must have confronted every teacher of physical chemistry. The student learns all too easily that "peevee equals enartee", but the apparent simplicity of the relations and the absence of concrete conceptions and numerical examples — to say nothing of absence of interest — combine to create a state of vagueness which will often hamper his progress for years. In order to overcome this difficulty the writer has constructed a simple model which has worked admirably, not only in giving students definite conceptions of Carnot's cycle, etc., but also in awakening their interest in, and aiding them to grasp, the essential idea of the calculus.

The model described below is, of course, only one of many possible arrangements which are not difficult to invent on paper, but this one has the advantage of having been actually tried and used by students, and this seems a sufficient reason for publishing its description. It can be constructed with about a day's work by any amateur mechanic.

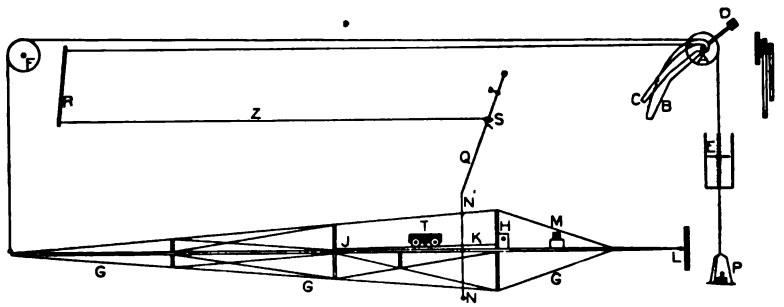

Fig. 1

It may be objected that the model is more complicated than

the laws it is intended to elucidate. To this it may be answered that if it were *not* so the students would pass it over as lightly as they do the laws themselves.

The model is set up on the vacant wall of a laboratory where students may work with it without interference from instructors. The essential part of the apparatus is a circular wooden pulley A, 20 cm in diameter, to which is fixed rigidly a wooden curve B, the co-ordinates of which are given in Table I, and which, together with the second curve (mentioned below), is exactly counterbalanced by the weight D. The curves are made of 3/8-inch pine and carry double rows of ordinary pins on the edge which act as flanges. The whole is pivoted with brass bearings on a horizontal steel pin. At a suitable point on A is fixed an iron wire (No. 24, B. & S.) which carries a pan P at its lower end. A tin cross-piece is attached to the wire at a convenient height from the ground to represent a piston, behind which is a piece of cardboard bearing a diagram of a cylinder and a millimeter scale. To the right hand end of the curve B a piece of strong thread is fastened, which passes round the curve to a pulley F, similar to A, and thence downwards to the end of the lever G, pivoted at H. This lever is made of a strip of light wood, about 4 meters long, and is braced with wire, as shown in the diagram, and also in the horizontal plane. It is counterbalanced by the weight M and is strong enough to carry a 5 kg weight at T. This weight rests on a toy wagon which may be moved along a flat board between J and K. On the edge of this board, which is in such a position that the centre of gravity of the weight remains in a line with the end of the lever and the fulcrum, is pasted a millimeter scale, numbered from the fulcrum as zero.

The curve B fulfils the condition that the length of the perpendicular from the centre of revolution to the horizontal tangent is inversely proportional to the angle through which the curve is moved. It is part of an infinite spiral, and was obtained graphically as the envelope of a suitable number of tangents. The position of the bottom of the cylinder (vol. = o) may be found by turning the curve to the position in which the y-axis

(see table) is horizontal. This corresponds to the angle of revolution taken as zero, in drawing the curve. The distance of A from F, about 5 meters, is such that the thread remains practically horizontal.

This arrangement gives the relation between pressure, volume, and temperature,

$$pv = nRt.$$

The pressure in grams is the weight on the pan P, *plus* the weight of the pan which is 100 g. The volume is the distance of E from the bottom of the cylinder, and the absolute temperature is the distance, in millimeters, of a pointer at the centre of gravity of the wagon T from the fulcrum H. For the dimensions and weight given, the value of n is 0.000317 g-mol and the limits of volume are in the ratio of 1 to 5.

The work done in compressing the gas isothermally is equal to the work required to raise the weight T, and therefore the scale L (which is 1400 mm from the fulcrum) gives the value of const. log v + const. If d is the reading in centimeters on this scale,

$$\text{work} = 5000 \frac{t}{1400} d \text{ g-cm}.$$

The additional restriction imposed on the variability of p, v, and t for *adiabatic* changes is supplied by the following arrangement. To the wheel A is fixed a second curve C which fulfils the following condition :

$$s = \frac{\text{const}}{a^{k-1}},$$

where s is the horizontal movement of a tangential thread, a the angle of rotation, and k the ratio Cp/Cv.

If l is the length of the perpendicular from the centre of revolution to the horizontal tangent, then

$$l = \frac{ds}{da} = \text{const}' a^{-k},$$

and consequently it was possible to obtain this curve, graphically, exactly as in the case of the one already described. The co-

ordinates of the curve for $k = 2$ are given in Table II.[1] The tangential thread[2] actuates the lever R and the pointer Q, made of a very light, thin glass tube properly counterbalanced, to the end of which is attached a plumb line N, N of fine cotton terminating in a small weight. Since R is at a distance of about five meters from C and Q, it is clear that the horizontal movements of the plumb line N represent the alteration of temperature for an adiabatic change of volume, v, or,

$$tv^{k-1} = \text{const.}$$

Since the pivot of Q is exactly over the zero of absolute temperature, H, the proper value may be given to the above constant for any adiabatic line by moving the connecting point S (a small piece of sheet rubber with a hole in it) up or down the glass pointer till N is opposite the pointer on the temperature wagon. To carry out an adiabatic expansion, therefore, it is simply necessary to set the pointer for the initial state by adjustment of the point S, and then to keep the temperature wagon opposite N during the alterations of pressure. It is necessary, of course, after setting up the model, to adjust the length of the fiber Z, so that at infinite volume the adiabatic pointer will be at zero. This can be done by adjusting the fiber to any length, taking two pairs of readings of temperature and volume, and calculating what correction in length will satisfy the above equation.

The co-ordinates of the curves B and C are given in the following tables. The values are expressed in centimeters. For both curves the centre of revolution is $x = 10$, $y = 12.5$ and the tangent for vol. $= 0$ is parallel to the y-axis.

[1] The value 2 was chosen rather than an actual value for some known gas, both to simplify the calculations and also to avoid the extreme slenderness of the p, v-diagram of an actual Carnot's cycle.

[2] Owing to the necessary lightness of the pointer and plumb line, the "sag" even of the finest cotton introduces an error. For this reason fine glass fibers were used for working the adiabatic pointer and found quite satisfactory. They can be attached to pieces of cotton, at the two ends, by strips of gummed paper.

TABLE I. (Curve B)

x	y	x	y
10.8	8.7	4.5	17.7
10.0	8.45	5.4	19.4
9.1	8.4	6.7	21.0
8.15	8.5	8.5	22.4
7.25	8.75	11.1	23.7
6.40	9.2	14.0	24.5
5.5	9.95	18.1	24.9
4.8	10.9	23.3	24.3
4.25	11.9	30.0	22.2
3.9	13.0	38.5	17.5
3.8	14.3	49.5	8.4
4.0	16.0	57.5	0.0

TABLE II. (Curve C)

x	y	x	y
10.2	12.0	17.7	18.7
10.0	11.87	21.0	18.5
9.7	11.8	23.5	18.1
9.3	11.9	27.0	17.1
8.9	12.2	30.2	16.0
8.6	12.7	38.6	11.9
8.4	13.6	49.0	5.5
8.7	14.7	55.5	0.4
9.8	16.2	—	—
11.2	17.2	—	—
12.6	17.9	—	—
15.0	18.5	—	—

In conclusion, a few examples of the problems illustrated by the model may not be out of place.[1]

A Carnot's cycle process was carried out between the absolute temperatures 483° and 360°, and a number of points were plotted in pressure-volume co-ordinates on millimeter paper. The various areas were cut out, weighed, and compared with a square of paper of known size. The work gained during the cycle was calculated by the following methods:

[1] The numbers and calculations were supplied by two second year students, Messrs. T. B. Allen and R. A. Daly.

(1) Weight of area enclosed by the two isothermals and two adiabatics, 0.2320 g, corresponding to 1850 g-cm.

(2) Weights of areas representing work done during isothermal expansions at 483° and 360,°, respectively,
0.8965 g, corresponding to 7156 g-cm
and 0.6697 g, " " 5346 "
Difference .. .. 1810 g-cm.

(3) $\frac{T' - T''}{T'} Q_1 = \frac{483 - 360}{483} 7156 =$ ..... 1822 g-cm.

(4) $0.000317\ R\left(483 \log_n \frac{28.0}{16.2} - 360 \log \frac{37.0}{21.4}\right) = 1636$ g-cm.

The work done during the isothermal expansion at 483°, calculated *directly* from *weight of wagon* (4855 g) × distance raised (determined from movement of pointer, 4.13 cm, on scale L, in figure) was:

$$4855 \frac{483}{1400} \cdot 4.13 = 6916 \text{ g-cm (compare value above, 7156 g-cm.)}$$

The equality of the amounts of work done during the two adiabatic expansions is illustrated by the weights of the corresponding areas of paper:

0.3993 g and 0.4045 g.

The values of the constant R, calculated from various points, taken at random, from the above-mentioned curves, are

85310, 85190, 83710, 85150, 84740.

The constancy of pv^k is illustrated by the values calculated for three points on one of the adiabatics:

21250, 21100, 20820.

It will be noticed that the model is not perfect; but the same may be said of gases.

University of Toronto,
Chemical Laboratory,
April, 1904.

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No. 48. THE RATE OF THE REACTION BETWEEN IODIC AND HYDRIODIC ACIDS, BY S. DUSHMAN

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THE RATE OF THE REACTION BETWEEN IODIC AND HYDRIODIC ACIDS

BY SAUL DUSHMAN

In 1888 the rate of reaction between iodic and hydriodic acids was made the subject of a research by O. Burchard,[1] who endeavored to discover a relation between the rate and the concentrations of these two reagents. His results, however, were unsatisfactory, and the author concludes his paper with the words, "In spite of all attempts, I have not succeeded in representing the rate of the reaction by a general differential equation".

In light of the electrolytic dissociation theory introduced by Arrhenius just at the time of Burchard's publication, it now seems advisable to represent hydrogen iodide in solution as consisting almost entirely of hydrion ($\overset{+}{H}$) and iodion ($\overset{-}{I}$); similarly a solution of iodic acid contains hydrion ($\overset{+}{H}$) and iodation ($\overset{-}{IO_3}$), while brown "iodine" solution contains tri-iodion ($\overset{-}{I_3}$).

Thus, in place of Burchard's equation,

$$5HI + HIO_3 = 3I_2 + 3H_2O, \qquad (1)$$

it seems better to write

$$6\overset{+}{H} + 8\overset{-}{I} + \overset{-}{IO_3} = 3\overset{-}{I_3} + 3H_2O, \qquad (2)$$

and in consequence, I have studied the effect of the concentrations of $\overset{+}{H}$, $\overset{-}{I}$, $\overset{-}{IO_3}$ and $\overset{-}{I_3}$ on the rate, instead of adopting the variables chosen by Burchard.

In planning the experiments, I adopted a method which was originally employed by Harcourt and Esson in their classical research, "On the Observation of the Course of Chemical Change", in 1866,[2] but which had, apparently been completely forgotten by 1888. The principle of the method is very sim-

[1] Zeit. phys. Chem. 2, 796 (1888).

[2] Jour. Chem. Soc. 20, 476 (1867).

ple, and consists in keeping the concentrations of all the reagents but one constant, or almost constant, during the progress of the reaction; any change in the rate must then be ascribed to changes in the concentration of that one substance only. In Burchard's work on the other hand, the concentrations of all the reagents changed during every experiment, and he was unable to discover the effect due to each.

In the investigations of Harcourt and Essen, and in those carried on in this laboratory by Messrs. Bray,[1] Bell,[2] Roebuck,[3] DeLury,[4] Forster,[5] and Miss Benson,[6] the concentrations of all the reagents except one were *held constant by employing relatively high concentrations of the reagents in question.* In my preliminary experiments I made up the solutions on the same plan, using a small amount of potassium iodate (iodation), and large excesses of potassium iodide (iodion) and hydrochloric acid (hydrion). I soon found, however, that the solutions had to be much diluted in order to make the rate of the reaction slow enough to measure, and that in these very dilute solutions accurate analytical determination of the iodine liberated was impossible.

Finally I replaced the excess of hydrochloric acid by excess of acetic acid and sodium acetate, thus obtaining solutions in which *the concentration of the hydrion, though lower than those of the iodation and iodion, remained unaltered* throughout the experiment. In the acetic acid solutions the rate was much slower than in those containing hydrochloric acid, great dilution was not necessary, and the analytical difficulties referred to above were avoided.

Experiments in which the concentrations of the reagents were systematically varied led to very simple results, namely, that the rate of the reaction between hydriodic and iodic acids

[1] Jour. Phys. Chem. 7, 92 (1903).
[2] Ibid. 7, 61 (1903).
[3] Ibid. 6, 365 (1902).
[4] Ibid. 7, 239 (1903).
[5] Ibid. 7, 640 (1903).
[6] Ibid. 7, 1 (1903).

is proportional to the concentration of the iodation, to the square of the concentration of the hydrion, and to the 1.8th or 1.9th power of that of the iodion, while the tri-iodion exerts an accelerating influence which was studied in detail. By means of the differential equation embodying these relations, I was able to predict the course of the reaction in solutions containing hydriodic and iodic acids only.

The results, apart from their intrinsic interest, are of value as showing the power of Harcourt and Esson's method in the study of Chemical Kinetics. As recently as 1898, in a paper on "The Reduction of Bromic Acid and the Law of Mass Action",[1] the authors, Messrs. Judson and Walker, expressed themselves as follows: "It is evident, therefore, that the action of hydriodic acid on the oxygen acids of the halogens is of too intricate a nature to give any satisfactory numerical results". The rate of this "intricate reaction" is now known as a simple function of the concentrations of the reagents involved.

METHOD OF WORKING

Precautions taken to exclude air

As the unsatisfactory outcome of Burchard's investigation has been ascribed in part to the action of atmospheric oxygen on his solutions, I took special precautions to exclude air during the work. Pairs of experiments, however, in one of which the air was excluded, while in the other it was allowed access, seemed to show that the error arising from this source was negligible.

All the solutions used in the experiments were prepared free from air by boiling and cooling in vacuo, and were kept under carbonic acid gas, which was purified by passing through water, solutions of sulphuric acid, ferrous sulphate, and permanganate of potassium, and through a long tube filled with cotton wool.

Before removing a solution from one of the stoppered flasks clamped in the thermostat (see below), the pipettes were filled

[1] Jour. Chem. Soc. 73, 411 (1898).

with carbon dioxide, and a current of the gas was passed into the flask as long as the stopper was out.

Description of an experiment

The main stock of the solutions of potassium iodide, potassium iodate, acetic acid and sodium acetate was kept in bottles under carbon dioxide, as already stated; and before each series of experiments about 200 cc of each were brought to 0° C in stoppered flasks (clamped in the thermostat) from which the air had been removed by a current of carbon dioxide. The thermostat was also provided with a large test-tube (100 cc capacity) and a 500 cc beaker with stirring rod.

Each measurement contained in the following tables involved the preparation of a new reacting mixture, as follows: Into the test-tube was first pipetted air-free water in quantity sufficient (together with that of the reagents subsequently added) to make up the total volume to 100 cc; measured quantities of sodium acetate, acetic acid and potassium iodide solutions were then added. The potassium iodate was measured into the beaker and the stirrer set in motion, the contents of the test-tube were then thrown in, and at the same instant the catch of a stop-watch was released by means of a pedal. Experiments with colored solutions showed that a homogeneous mixture was attained in from one-fifth to one-half second. When it was desired to interrupt the reaction, the contents of the beaker were again stirred rapidly, about 10 cc of ammonium bicarbonate solution thrown in from a test-tube and the watch stopped. The iodine liberated was then determined with centinormal sodium arsenite and iodine solutions, using starch as an indicator.[1] Duplicate experiments gave results agreeing within 0.10 cc of the volumetric arsenite solution, while duplicate analyses of the same mixture agreed within 0.05 cc.

All pipettes and burettes used in these measurements were freshly calibrated, the pipettes by weighing the distilled water discharged at 4° C, and the burettes as described in Ostwald's

[1] For the method of analysis of the mixture in presence of excess of iodine, see page 468.

" Hand- und Hilfsbuch," page 103. In using the pipettes 45 seconds were allowed for draining.

Solutions employed

Water. — All the water used in these experiments was freed from air, and kept under carbon dioxide.

Potassium iodate. — 0.00918-F,[1] and 0.00100-F KIO_3, prepared by dissolving weighed quantities of the salt, and standardized by decomposing a measured volume with excess of potassium iodide and hydrochloric acid, adding excess of ammonium bicarbonate, and titrating with 0.01049-*n* sodium arsenite.

Sodium acetate. — 0.10035-F, $C_2H_3O_2Na$, prepared by dissolving 13.6 grams of Merck's crystallized sodium acetate to one liter; a few crystals of menthol were added to prevent the growth of moulds. To standardize it, a measured volume was evaporated in a tared crucible at 100° C, the crucible and salt were then heated to 110°–120° for four hours, allowed to cool in a desiccator, and the anhydrous sodium acetate weighed.

Acetic acid. — 1.147-F, $C_2H_4O_2$, prepared by diluting Merck's " pure glacial acetic acid, 99.5 percent acid ", and titrating against standard potash.

Hydriodic acid. — 0.1128-F and 0.001132-F HI; prepared by diluting a stock solution made from water, iodine, and red phosphorus; titrated against the standard potash. These solutions contained a little free iodine, which was determined by sodium arsenite (20 cc of the 0.1128-F HI took 0.42 cc of 0.0105-*n* arsenite), and in each measurement in which hydriodic acid was used, the small correction for the free iodine was made at the time of the analysis.

Iodic acid. — 0.00976-F and 0.00100-F HIO_3. Large, colorless crystals of iodic acid, free from sulphuric acid (prepared by oxidizing iodine with nitric acid, sp. gr. 1.53) were dissolved, and the solutions standardized by sodium arsenite (see under Potassium iodate).

Iodine and potassium iodide. — Twenty-five cc was equiva-

[1] Formula-weights per liter.

lent to 21.77 cc 0.1049-*n* arsenite, hence 0.04567-F tri-iodion, I_3^-. After boiling off the free iodine, 50 cc with silver nitrate gave 1.1387 g AgI, hence 0.0970-F KI. Since each mol of iodine (I_2) reacts with one of potassium iodide (iodion, $\bar{I}$) to form one of potassium tri-iodide (tri-iodion, $\bar{I}_3$) the formation of 0.04567 mol $\bar{I}_3$ per liter has used up 0.04567 mol iodion, leaving 0.0970 — 0.04567 = 0.05133 mol iodion ($\bar{I}$) per liter.

Iodine and hydriodic acid. — The 0.1128-F hydriodic acid was saturated with iodine, and the "free iodine" (tri-iodion) determined by sodium arsenite and found to be 0.0415-F I_3^-. Subtracting 0.0415 from 0.1128 there remains the concentration of the iodion, 0.0713-F, while the hydrion is 0.1128-F $\dot{H}$.

Volumetric sodium arsenite. — 0.01049-normal; standardized with dry, freshly sublimed iodine. The *volumetric iodine solutions* were compared daily with the arsenite; and the *volumetric sodium thiosulphate* was standardized against the iodine solutions.

The half saturated *ammonium bicarbonate* solution was kept under CO_2. A distinct blue coloration was obtained when one drop of centinormal iodine was added to a mixture of 100 cc water, 10 cc ammonium bicarbonate solution, 2 cc starch solution, and a few drops of normal potassium iodide.

RESULTS OF THE EXPERIMENTS

Explanation of the Tables (Series I and II)

At the head of each table is given the initial composition of the reacting mixture. The numbers following each formula denote the number of gram-formula-weights of that reagent in 100 cc of reacting mixture. Thus IO_3^-, 0.000025; I, 0.00177; HAc, 0.00585; NaAc, 0.0015 (at the head of Table 1) means that 25 cc of 0.0010-F KIO_3, 20 cc of 0.0885-F KI, 5 cc of 1.17-F HAc, 15 cc of F/10 NaAc were made up to a volume of 100 cc. From the numbers after HAc and NaAc, was calculated the quantity of hydrion, $\dot{H}$, in the mixture, assuming the dissocia-

tion constant of acetic acid to be 0.000018,[1] and the sodium acetate to be totally dissociated; thus for HAc 0.00585, and NaAc 0.0015 (V 0.1 liter).

$$KV(\mathrm{HAc}) = \overset{+}{\mathrm{H}} \times \overline{\mathrm{Ac}}$$

$$0.000018 \times 0.1 \times 0.00585 = \overset{+}{\mathrm{H}} \times (\overset{+}{\mathrm{H}} + 0.0015),$$

whence $\overset{+}{\mathrm{H}} = 0.000007$

Under "t" is entered the time in minutes during which the mixture was allowed to react, and under "*As*" the number of cc of the volumetric sodium arsenite equivalent to the iodine liberated. In the third column are entered the values k_1 or k_2.

$$k_1 = \frac{1}{t} \log_{10} \frac{IO_3}{IO_3 - x}, \quad \text{.....(I)}$$

$$k_2 = \frac{1}{t} \left(\frac{1}{I - y} - \frac{1}{I} \right) \quad \text{.....(II)}$$

To obtain x, the number of mols of IO_3 reduced for each cc of *As*, the burette readings must be multiplied by 0.00000175. (1 cc *As* = 0.00001049 equivalent; 1 mol IO_3 gives 6 equivalents of iodine.)

To obtain y, the number of mols of $\overline{\mathrm{I}}$ corresponding to 1 cc of *As* in the titration, the burette readings must be multiplied by 0.00001398. (From equation (2)

8 KI yields 3 KI_3 = 6 equivalents of iodine,

or for each mol of KI destroyed, 3/8 mol of KI_3 is formed, that is, 3/4 equivalent of *As* is used in titration. Hence, 1 cc *As* = 4/3 × 1/1000 × 0.01049 = 0.00001398 mol KI.)

SERIES I. ACETIC ACID SOLUTIONS, POTASSIUM IODATE PRESENT IN SMALL QUANTITY

Effect of Iodation

The constancy of k_1 in each of the tables of this series shows that the rate is proportional to the concentration of the potassium iodate (iodation) in the reacting mixture. This conclusion is confirmed by the fact that doubling the concentration

[1] From the data and formulas of Arrhenius' paper (Zeit. phys. Chem. 4, 106) it appears that at 0° C the dissociation constant of acetic acid is below 0.00017. The hydrion concentrations given at the heads of Tables 1–27 are therefore all somewhat too high. See, however, page 474.

of the iodate does not affect k_1 (Tables 2 and 1). The slight falling off of k_1 in Table 2 is to be expected, as the concentration of the iodide is in relatively small excess.

Effect of Hydrion

From a comparison of Tables 1 and 3, and 1 and 4, it is apparent that the rate is proportional to the square of the concentration of the hydrion. In the first pair, the concentration of the hydrion was changed by doubling the concentration of the acetic acid, and in the second pair by doubling that of the sodium acetate. In Table 5 the concentration of both acid and salt is double that in Table 1, but the rate remains the same, thus affording a striking confirmation of the view that it is the concentration of hydrion that is effective.

Effect of Iodion

The effect of the concentration of iodion is not quite so simple. From Tables 1 and 6, 7 and 4, it is seen that doubling the concentration of the potassium iodide (iodion) multiplies the rate by $2^{1.85}$ or $2^{1.9}$. From Tables 9 and 10 we see that varying the concentration of iodion from 0.00886 to 0.000886 mol per liter, does not cause any variation in the exponent. It can, however, be seen from Table 10, and it will be more apparent from Series II, that the lower the concentration of iodion, the nearer the proportionality is between the rate and the square of its concentration. The other tables of this series show that the effects of the acid, acetate, and iodide are each independent of the others as well as of the iodate.

TABLE 1

IO_3, 0.000025; I, 0.00177; HAc, 0.00585; NaAc, 0.0015; H, 0.0000070

t	As	$k_1 \times 10^3$
2	1.13	17.9
4	2.24	18.5
6	3.15	18.0
8	4.15	18.6
10	4.87	18.6
		Av. 18.3

TABLE 2

IO_3, 0.000050; I, 0.00177; HAc, 0.00585; NaAc, 0.0015; H, 0.000007

t	As	$k_1 \times 10^3$
2	2.20	17.4
2	2.26	17.9
4	4.04	16.8
6	6.09	17.3
8	7.24	15.8
		Av. 17.3

TABLE 3

IO_3, 0.000025; I, 0.00177; HAc, 0.0117; NaAc, 0.0015; H, 0.000014

t	As	$k_1 \times 10^3$
1	2.30	76.2
2	4.17	75.0
2	4.14	74.4
2.5	4.78	71.0
4	6.87	71.2
6	8.76	68.7
		Av. 72.6

TABLE 4

IO_3, 0.000025; I, 0.00177; HAc, 0.00585; NaAc, 0.0030; H, 0.0000035

t	As	$k_1 \times 10^3$
2	0.34	5.3
4	0.62	4.8
6	0.89	4.7
8.5	1.22	4.6
10	1.54	4.9
		Av. 4.8

TABLE 5

IO_3, 0.000025 ; I, 0.00177 ; HAc, 0.0117 ; NaAc, 0.0030 ; H, 0.000007

t	As	$k_1 \times 10^3$
2	1.22	19.4
4	2.27	18.8
6	3.21	18.4
8	4.35	19.7
		Av. 19.1

TABLE 6

IO_3, 0.000025 ; I, 0.00354 ; HAc, 0.00585 ; NaAc, 0.0015 ; H, 0.000007

t	As	$k_1 \times 10^3$
2	3.86	68.4
3	5.16	64.8
4	6.50	65.9
6	8.18	61.5
8	9.62	60.7
		Av. 64.3

TABLE 7

IO_3, 0.000025 ; I, 0.00354 ; HAc, 0.00585 ; NaAc, 0.0030 ; H, 0.0000035

t	As	$k_1 \times 10^3$
2	1.17	18.5
4	2.19	18.1
6	3.20	18.3
8	3.93	17.5
10	4.78	17.6
		Av. 18.0

TABLE 8

IO_3, 0.000025 ; I, 0.00354 ; HAc, 0.0117 ; NaAc, 0.0015 ; H, 0.000014

t	*As*	$k_1 \times 10^3$
1	6.03	236.0
1.5	7.96	235.8
1.75	8.89	241.5
2	9.54	239.0
		Av. 238.2

TABLE 9

IO_3, 0.000025 ; I, 0.00885 ; HAc, 0.00585 ; NaAc, 0.0015 ; H, 0.000007

t	*As*	$k_1 \times 10^3$
1	8.64	403.2
1.25	9.66	391.5
1.50	10.46	381.2
1.75	11.24	383.4
		Av. 389.8

TABLE 10

IO_3, 0.000025 ; I, 0.000885 ; HAc, 0.00585 ; NaAc, 0.0015 ; H, 0.000007

t	*As*	$k_1 \times 10^3$
2	0.32	4.9
4	0.57	4.4
6	0.96	5.0
8	1.25	5.0
10	1.45	4.6
		Av. 4.8

SERIES II. ACETIC ACID SOLUTIONS, POTASSIUM IODIDE PRESENT IN SMALL QUANTITY

Effect of Iodion

The constancy of k_2 in each of the tables of this series shows that the effect of iodion varies as the square of its concentration when it is present in small quantity relatively to the iodate. In confirmation of this conclusion, we find that Table 12, in which the concentration of the iodide (iodion) is doubled, gives approximately the same constant as Table 11.

Effect of Iodation

Table 13 shows that doubling the concentration of the potassium iodate (iodation) multiplies the rate by 2; hence, as in Series I, the rate varies with the first power of the concentration of the iodation.

Effect of Hydrion

Tables 11 and 14, and 11 and 15, show that halving or doubling the concentration of the hydrion multiplies the rate by ¼ or 4 respectively. Tables 11 and 16 show that if the concentration of both acid and acetate be doubled, the rate remains unchanged. Hence, as in Series I, the rate is proportional to the second power of the concentration of the hydrion.

TABLE 11

IO_3, 0.000225; I, 0.00018; HAc, 0.0117; NaAc, 0.0015; H, 0.000014

t	As	k_2
4	1.06	125
6	1.46	120
8	1.84	116
12	2.69	122
15	3.07	116
		Av. 120

TABLE 12

IO_3, 0.000225 ; I, 0.00036 ; HAc, 0 0117 ; NaAc, 0.0015 ; H, 0.000014

t	*As*	k_2
1	1.04	119
2	1.86	109
3	2.72	110
4	3.46	108
		Av 112

TABLE 13

IO_3, 0.00045 ; I, 0.00018 ; HAc, 0 0117 ; NaAc, 0.0015 ; H, 0.000014

t	*As*	k_2
2	0.99	232
3	1.44	233
4	1.92	241
6	2.60	234
8	3.14	227
		Av. 235

TABLE 14

IO_3, 0.000225 ; I, 0.00018 ; HAc, 0.0117 ; NaAc, 0.0030 ; H, 0.000007

t	*As*	k_2
16	1.10	33
24	1.45	29
		Av. 31

TABLE 15

IO_3, 0.000225 ; I, 0.00018 ; HAc, 0.0234 ; NaAc, 0.0015 ; H, 0.000028

t	As	k_2
2	1.64	406
3	2.43	452
4	3.05	432
		Av. 442

TABLE 16

IO_3, 0.000225 ; I, 0.00018 ; HAc, 0.0234; NaAc, 0.0030 ; H, 0.000007

t	As	k_2
4	1.10	130
6	1.45	120
8	1.73	108
12	2.58	112
		Av. 117

Representation of the results by a differential equation

The results of the measurements of Series I and II may thus be stated in the following words :

"The rate of the reaction between iodation, iodion, and "hydrion, is proportional to the first power of the concentra- "tion of the iodation, to the 1.85th to second power of that "of the iodion, and to the second power of the concentration "of the hydrion."

Or, expressed in the form of a differential equation,

$$\frac{dx}{dt} = K\left(\frac{IO_3 - x}{V}\right)\left(\frac{I - y}{V}\right)^{1.9}\left(\frac{H}{V}\right)^2 \quad \text{.....(A)}$$

where $y = 8x$, and V is the volume in liters.

From the definitions of k_1 and k_2 on page 19, it follows that

$$K = 2.303\, k_1 V^4/(I)^{1.9}(H)^2 \quad \text{.....(B)}$$

$$K = k_2 V^5/(IO_3)(H)^2 \quad \text{.....(C)}$$

The following table contains the value of K for each of the foregoing tables, calculated by means of equations (B) and (C). Its constancy is a measure of the accuracy of equation (A). Physically interpreted, K represents the calculated number of mols of iodate that should be reduced in one minute when 1 mol of potassium iodide, 1 mol iodate, and 1 mol hydrion were present in a volume of 1 liter.

TABLE 17

No.	$IO_3 \times 10^5$	$I \times 10^5$	$H \times 10^6$	2303 k_1	k_2	$K \times 10^{-10}$
1	25	177	7.0	42	—	2.47
2	50	177	7.0	39	—	2.30
3	25	177	14.0	167	—	2.46
4	25	177	3.5	11	—	2.59
5	25	177	7.0	44	—	2.59
6	25	354	7.0	138	—	2.34
7	25	354	3.5	41	—	2.59
8	25	354	14.0	548	—	2.12
9	25	885	7.0	896	—	2.47
10	25	89	7.0	11	—	2.59
11	225	18	14.0	—	120	2.73
12	225	36	14.0	—	112	2.56
13	450	18	14.0	—	235	2.70
14	225	18	7.0	—	31	2.82
15	225	18	28.0	—	442	2.55
16	225	18	14.0	—	117	2.68
						Av. 2.54

SERIES III. ACETIC ACID SOLUTIONS, IODINE (TRI-IODION) PRESENT IN EXCESS

It is obvious, that owing to the excess of iodine put into the reacting mixture, it was not possible to make up solutions in which the quantity of potassium iodide was relatively small. Consequently in all the experiments of the present series the potassium iodate was selected as the substance to be present in small quantity.

In the measurements of this series a measured volume of decinormal iodine solution was mixed with the potassium iodate in the beaker (see "Description of an experiment," p. 456), and

water was added to bring the total volume up to 100 cc. Owing to the fact that the iodine liberated during the reaction was very small in amount compared with that initially present, the progress of the reaction was followed by estimating the residual potassium iodate instead of by trying to determine the small increase in the free iodine. The method has been worked out by Mr. Forster.[1]

Method of Analysis

The reaction was stopped by throwing in the ammonium bicarbonate, as before; sodium arsenite solution (0.1049-*n*) was run in from a burette, and then a little starch solution to determine the end-point. Thrice normal hydrochloric acid was next added in quantity sufficient to neutralize the sodium acetate, the ammonium bicarbonate, and the volumetric sodium arsenite, and to leave an excess of 2 cc of the 3-*n* hydrochloric acid. In solutions of this degree of acidity the potassium iodate was immediately reduced with liberation of an equivalent quantity of iodine, which was then determined by 0.01054-*n* sodium thiosulphate.

Blank experiments showed that the results are accurate within 0.10 cc (two drops of the volumetric sodium thiosulphate solution), but it is necessary to complete the titration within five minutes or iodine will be liberated by the action of the arsenic acid formed from the volumetric arsenite.

Explanation of the Tables

The symbols IO_3, HAc, NaAc, H, I, t, k_1'[2] have the meanings assigned on page 458. After KI is given the number of mols of potassium iodide, and after "Iod" the number of cc of the iodine solution added in making up the reacting mixture. In the brackets are given the number of mols iodion ($\bar{I}$) and triiodion ($\bar{I}_3$) contained in the iodine solution. The total quantity of iodion present in the reacting mixture is thus the sum of the

[1] Jour. Phys. Chem. 7, 640.

[2] In the tables of this series k_1' has been written instead of k_1, to distinguish the tables of this series from those of Series I.

numbers after KI and I. Under "Th" is given the number of cc of 0.01054-*n* sodium thiosulphate solution equivalent to the iodine liberated from the residual potassium iodate. In order to obtain $IO_3 - x$, used in calculating k_1', these burette readings must be multiplied by 0.000001744.

Effect of Iodation

From the constancy of k_1' in each of the tables of this series and by comparing Tables 20 and 23 (in the latter of which the concentration of the potassium iodate was double that in the former) it is apparent that the rate is proportional to the first power of the concentration of the iodation, and that the law according to which the iodation affects the rate is not modified by the presence of tri-iodion.

Effect of Hydrion

By comparing Tables 20, 22 and 25 it is evident that the rate is proportional to the square of the concentration of the hydrion. Thus the law according to which the hydrion affects the rate is not modified by the presence of tri-iodion.

Effect of Tri-iodion and of Iodion

The effect of tri-iodion might have been determined by comparing the experiments of this series with others in which the composition of the reacting mixture was the same except as regards the tri-iodion. Instead of undertaking a new series of measurements for this purpose, however, I have utilized those of Series I, making a correction for the small difference in the concentration of the iodion by assuming that k_1 is proportional to the 1.9th power of the concentration of the iodion (see page 460). In Table 18 are entered the compositions of the solutions of Tables 19 to 27, and the values of k_1'; also under k_1 the constants from the corresponding tables of Series I, corrected as described. The difference $k_1' - k_1$, which expresses the effect of tri-iodion on the rate, is roughly proportional to the concentration of the tri-iodion, to somewhat more than the second power of that of the hydrion, and to slightly less than the first power of the iodion.

TABLE 18

No.	$IO^3 \times 10^6$	$I \times 10^6$	$H \times 10^6$	$I_3 \times 10^5$	$k_1' \times 10^3$
19	25	2053	7.0	183.0	38.6
20	25	1911	7.0	91.5	27.6
21	25	1841	7.0	45.7	23.6
22	25	1911	14.0	91.5	121.4
23	50	1911	7.0	91.5	29.1
24	25	3682	7.0	91.5	79.5
25	25	1911	3.5	91.5	7.3
26	25	3611	7.0	45.7	72.1
27	25	3820	7.0	183.0	97.2

No.	$k_1 \times 10^3$	$k_1' - k_1 \times 10^3$	Q	$k_1' \times 10^3$ *calc.*	Diff.
19	24.3	14.3	7.8	37.3	− 3.4 %
20	20.8	6.8	7.9	27.3	− 1.1
21	19.8	3.8	9.0	22.9	− 1.7
22	82.8	38.6	(12.5)	108.8	−10.0
23	19.7	9.4	(10.9)	26.2	−10.0
24	69.3	10.2	6.2	81.8	+ 4.0
25	5.5	1.8	7.8	7.1	− 3.0
26	66.7	5.4	6.7	72.8	+ 1.0
27	74.3	22.9	6.7	100.3	+ 3.0
			Av. 7.4		

The quotient,

$$Q = \frac{(k_1' - k_1)\, V^4 \times 10^{-9}}{(I_3) \times (H)^2 \times (I)},$$

is thus approximately constant, the average value being 7.4. Using this value, I calculate k_1' for each of the Tables 19 to 27.

$$k_1' \text{ calc} = k_1 + 7.4 \times (I_3) \times (H)^2 \times (I) \times 10^{13} \ldots\ldots \text{(D)}$$

The difference between the calculated and observed values of k_1' expressed as percent of the latter, is entered under "Diff." With the exception of Tables 22 and 23, the greatest discrepancy is 4 percent, well within the experimental errors. In the case of Tables 22 and 23 the difference amounts to 10 percent; k_1' for Table 22 is, however, very uncertain (page 472), and if the average of k_1' for Tables 23 and 20 be entered instead of k_1' for each of them, the discrepancy between observed and calculated values of k_1' is reduced to 6 percent.

Representation of the results by a differential equation

$$dx/dt = k_1'(IO_3)/V \times 2.303 \quad \text{(p. 469)}$$

$$k_1' = k_1 + 7.4 \times 10^9 \times (I_3) \times (I) \times (H)^2 \times 1/V^4 \quad \text{(D, p. 470)}$$

$$k_1 = \frac{K \times I^{1.9} \times (H)^2}{2.303 \times V^4} \quad \text{(B, p. 466)}$$

$$\text{Let } R = 7.4 \times 10^9 \times 2.303 \quad \text{(E)}$$

Then the general differential equation may be written

$$\frac{dx}{dt} = K\left(\frac{IO_3 - x}{V}\right)\left(\frac{I - y}{V}\right)^{1.9}\left(\frac{H}{V}\right)^2 + R\left(\frac{IO_3 - x}{V}\right)\left(\frac{I - y}{V}\right)\left(\frac{I_3}{V}\right)\left(\frac{H}{V}\right)^2 \quad \text{(F)}$$

or more simply

$$\frac{dx}{dt} = \frac{(IO_3)\cdot(I)\cdot(H)^2\{K(I)^{0.9} + R(I_3)\}}{V^5} \quad \text{(G)}$$

where

$$K = 2.54 \times 10^{10} \quad \text{(p. 467)}$$

$$R = 1.70 \times 10^{10} \quad \text{(E)}$$

TABLE 19

IO_3, 0.000025 ; Iod, 40 cc ; (I_3, 0.00183 ; I, 0.002053); HAc, 0.0058 ; NaAc, 0.0015 ; H, 0.000007

t	*Th*	$k_1' \times 10^3$
2	11.85	41.3
4	10.04	38.6
6	8.75	36.0
		Av. 38.6

TABLE 20

IO_3, 0.000025 ; Iod, 20 cc ; (I_3, 0.000915 ; I, 0.0010265); I, 0.000885 ; HAc, 0.0058 ; NaAc, 0.0015 ; H, 0.000007

t	*Th*	$k_1' \times 10^3$
2	12.60	27.9
4	11.24	26.4
6	9.72	28.1
8	8.60	27.7
		Av. 27.6

TABLE 21

IO_3', 0.000025; Iod, 10 cc; (I_3', 0.000457; I, 0.0005133); I, 0.001328; HAc, 0.0058; NaAc, 0.0015; H, 0.000007

t	Th	$k_1' \times 10^3$
2	12.97	21.7
4	11.66	23.4
6	10.20	24.6
8	9.05	24.9
		Av. 23.6

TABLE 22

IO_3', 0.000025; Iod, 20 cc; (I_3', 0.000915; I, 0.0010265); I, 0.000885; HAc, 0.0117; NaAc, 0.0015; H, 0.000014

t	Th	$k_1' \times 10^3$
1	11.09	111.3
1.5	9.35	123.6
2	7.90	129.3
		Av. 121.4

TABLE 23

IO_3', 0.000050; Iod, 20 cc; (I_3', 0.000915; I, 0.0010265); I, 0.000885; HAc, 0.0058; NaAc, 0.0015; H, 0.000007

t	Th	$k_1' \times 10^3$
1	26.58	31.3
2	24.51	32.8
3	23.94	(24.7)
4	22.20	27.7
		Av. 29.1

TABLE 24

IO_3, 0.000025; Iod, 20 cc; (I_3, 0.000915; I, 0.0010265); I, 0.002655; HAc, 0.0058; NaAc, 0.0015; H, 0.000007

t	*Th*	$k_1' \times 10^3$
1	12.99	73.8
1.5	10.70	(84.5)
2	10.00	78.1
3	8.17	81.5
		Av. 79.5

TABLE 25

IO_3, 0.000025; Iod, 20 cc; (I_3, 0.000915; I, 0.0010265); I, 0.000885; HAc, 0.0058; NaAc, 0.0030; H, 0.0000035

t	*Th*	$k_1' \times 10^3$
8	12.56	7.1
16	10.88	7.4
		Av. 7.3

TABLE 26

IO_3, 0.000025; Iod, 10 cc; I_3, 0.000457; I, 0.0005133); I, 0.0030975; HAc, 0.0058; NaAc, 0.0015; H, 0.000007

t	*Th*	$k_1' \times 10^3$
1	12.24	68.5
2	10.09	76.2
3	8.62	73.5
4	7.51	70.2
		Av. 72.1

TABLE 27

IO_3, 0.000025; Iod, 40 cc; (I_3, 0.00183; I, 0.002053); I, 0.00177; HAc, 0.0058; NaAc, 0.0015; H, 0.000007

t	*Th*	$k_1' \times 10^3$
2	9.16	97.2

SERIES IV. SOLUTIONS OF HYDRIODIC AND IODIC ACIDS

Having determined the rates in solutions in which the components hydrion, iodion, and iodation, could each be controlled separately, it remained to carry out a few measurements with the acids themselves.

The results of these experiments are given in Tables 28 to 34, where the symbols used have the significance explained on page 458. The concentrations are given on the assumption that hydriodic and iodic acids are completely dissociated into their ions. In order to keep the rate within measurable limits only small quantities of each reagent could be used; the experimental errors in this series are therefore much larger than in the previous tables; but nevertheless the constants are very fair.

Before performing the experiments with the pure acids, the measurements of Series I to III were connected with those of the following series, by several determinations in solutions containing (i) acetic acid, sodium acetate, potassium iodate, hydriodic acid, and (ii) acetic acid, sodium acetate, potassium iodide, iodic acid, respectively. The results were in good agreement with the requirements of equation (A) page 466, and demonstrated the absence of catalyzers in the hydriodic and iodic acid solutions.

In Tables 28 to 31 the hydriodic acid was present in excess; in Tables 32 to 34 the iodic acid. The values of K (page 466) for all these experiments are collected in Table 35; with the exception of K for Table 33, they show fair agreement. The laws which have been discovered in the systematic experiments of the previous series thus hold also for solutions containing hydriodic and iodic acids only. The average value of K however (0.84) is much lower than that found with acetic acid solutions (2.54).

A small part of this difference may be ascribed to the assumption of total dissociation of the acids made in the calculation. Experiments in which sodium chloride was added to the acid solution (Table 36), without effect on the rate, show that the difference cannot be ascribed to acceleration by the sodium

ions introduced with the sodium acetate in the previous series.

If it be assumed that the rate is strictly proportional to the square of the concentration of the hydrogen-ion, there remains only the hypothesis that the calculation of the dissociation of acetic acid is faulty. If in Table 17 H be set, not 0.000007 but 0.000012, the agreement is good; this corresponds to a value 0.00003 for the dissociation constant of acetic acid, however, which is entirely out of the question (see page 459). This is not the first time that the calculation of dissociation from conductivity measurements has given unsatisfactory results.

TABLE 28

IO_3, 0.000005; I, 0.000564; H, 0.000569; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
2	0.74	65.0
4	1.28	64.4
5	1.44	61.0
7	1.70	56.0
		Av. 61.6

TABLE 29

IO_3, 0.000010; I, 0.000564; H, 0.000574; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
2	1.51	67.3
3	2.06	65.5
4	2.33	57.5
		Av. 63.4

TABLE 30

IO_3, 0.000005; I, 0.001128; H, 0.001133; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
0.25	1.66	(1568.7)
0.5	2.30	1216.4
1.0	2.58	1010.0
		Av. 1113.2

TABLE 31

IO_3', 0.000005 ; I, 0.000564 ; H, 0.000569 ; Vol, 0.39 liter

t	As	$k_1 \times 10^3$
4	0.81	36.1
8	1.37	33.0
		Av. 34.6

TABLE 32

IO_3', 0.0000488 ; I, 0.0000566 ; H, 0.0001054 ; Vol, 0.1 liter

t	As	k_2
4	0.45	540
8	0.84	578
		Av. 559

TABLE 33

IO_3', 0.0000976 ; I, 0.0000556 ; H, 0.0001542 ; Vol, 0.1 liter

t	As	k_2
2	1.02	2984
3	1.35	2956
4	1.60	2899
		Av. 2946

TABLE 34

IO_3', 0.0000488 ; I, 0.0001132 ; H, 0.0001620 ; Vol, 0.1 liter

t	As	k_2
2	1.60	1100
3	2.28	1114
4	2.56	1064
		Av. 1093

TABLE 35

No.	V	$IO_3 \times 10^6$	$I \times 10^6$	$H \times 10^6$
28	0.31	5.0	564.0	569.0
29	0.31	10.0	564.0	574.0
30	0.31	5.0	1128.0	1133.0
31	0.39	5.0	564.0	569.0
32	0.10	48.8	56.6	105.4
33	0.10	97.6	56.6	154.2
34	0.10	48.8	113.2	162.0

No.	$k_1 \times 10^3$	k_2	$K \times 10^{-10}$
28	61.6	—	0.62
29	63.4	—	0.64
30	1113.2	—	0.82
31	34.6	—	0.70
32	—	559.0	1.00
33	—	2946.0	1.25
34	—	1093.0	0.83
			Av. 0.84

TABLE 36

5 cc F/10 NaCl; IO_3, 0.000005; I, 0.000564; H, 0.000569; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
2	0.75	66.0
4	1.22	60.4
5	1.43	60.2
		Av. 62.2

TABLE 37

10 cc F/10 NaCl; IO_3, 0.000005; I, 0.000564; H, 0.000569; Vol, 0.31 liter

t	As	$k_1 \times 10^3$
2	0.70	61.0
4	1.21	60.0
5	1.45	61.4
		Av. 60.8

SERIES V. HYDRIODIC AND IODIC ACIDS, IODINE (TRI-IODION) PRESENT IN EXCESS

Tables 39 to 41 give the results of measurements with the solutions of hydriodic and iodic acids to which an excess of iodine was added in the form of hydrogen tri-iodide (HI_3). As the results of this series are in full agreement with those of Series III, I shall merely add the following table (38) to show that the effect of tri-iodion on the rate between the pure acids is governed by the same laws as its effect when in presence of neutral salts (sodium acetate and potassium salts in Series III). The meanings of the symbols are the same as in the tables of Series III. In order to facilitate comparison of Series V with Series IV, I have recalculated the corresponding values of k_1 in the former series for the same concentration of iodion as in Tables 39 to 41 (assuming that the rate is proportional to the square of the concentration of the iodion). These numbers are entered under k_1.

TABLE 38

No.	$IO^3 \times 10^6$	$I \times 10^6$	$H \times 10^6$	$I_3 \times 10^6$
39	5	356	569	208
40	10	356	574	208
41	5	712	1133	416

No.	$k_1' \times 10^3$	$k_1 \times 10^3$	$(k_1'-k_1) \times 10^3$	S
39	67.0	25.0	42.0	1.7
40	59.5	25.3	34.2	1.4
41	882.0	443.0	439.0	1.2
				Av. 1.4

The constancy of the quotient,

$$S = \frac{(k_1' - k_1) \times 10^{-12}}{(I_3) \times (H)^2 \times (I)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (H)$$

shows that the rate, in the presence of an excess of iodine, is proportional to the square of the concentration of the hydrion, to the first power of that of the iodion and to the first power of that of the tri-iodion.

The results of Series IV and V may thus be represented by the differential equations (F) and (G), of page 471, which served for Series I-III; the numerical values of K and R however, are different.

$K = 0.84 \times 10^{10}$ (instead of 2.54×10^{10}, page 471)

$R = 0.32 \times 10^{10}$ (instead of 1.70×10^{10}, page 471).

TABLE 39

IO_3, 0.00005; I, 0.00005; I_3, 0.000208; H, 0.000569; Vol, 0.31

t	Th	$k_1' \times 10^3$
1	2.37	81.7
2	2.15	62.0
2.5	1.90	71.0
5	1.33	66.5
7	1.20	54.0
		Av. 67.0

TABLE 40

IO_3, 0.000010; I, 0.000356; I_3, 0.000208; H, 0.000574; Vol, 0.31

t	Th	$k_1' \times 10^3$
2	4.35	59.5
3	4.00	(52.0)
		Av. 59.5

TABLE 41

IO_3, 0.000005; I, 0.000712; I_3, 0.000416; H, 0.001133; Vol, 0.31

t	Th	$k_1' \times 10^3$
0.5	1.13	807
0.75	0.59	914
1.0	0.34	925
		Av. 882

V. TEMPERATURE COEFFICIENT

The measurements of Table 1 (at 0° C) were repeated at a temperature of 37° C, and one measurement was made at 14° C. The results are given in Table 42.

TABLE 42

IO_3, 0.000025; I, 0.00177; HAc, 0.00585; NaAc, 0.0015; H, 0.000007

Temp.	t	As	$k_1 \times 10^3$	$K \times 10^{-10}$
37° C.	2	2.68	44.0	—
"	4	4.63	43.0	—
"	6	6.18	41.0	—
			Av. 42.6	5.90
14° C.	4	3.23	28.0	3.90
0° C.	–	—	18.3	2.54

The rate rises almost *linearly* with the temperature, a rise from zero to 10° C multiplying the rate by about 1.4. This is one of the lowest temperature coefficients on record.[1]

VI. EFFECT OF LIGHT AND OF CATALYZERS

Experiments with solutions of hydriodic and iodic acids in which, by means of a concave mirror, direct sunlight was concentrated on the reacting mixture in the beaker, gave the same results as those carried out in the diffuse light of the laboratory.

By means of a few measurements it was found that potassium bichromate does not affect the rate and that ferrous sulphate accelerates only moderately.

VII. MOLECULAR INTERPRETATION OF THE RESULTS

The form of the differential equation found above suggests the simultaneous occurrence of two reactions in solutions con-

[1] See DeLury. Jour. Phys. Chem. 7, 251 (1903).

taining iodide, iodate, acid and free iodine, corresponding to the chemical equations

(i) $$2\bar{I} + 2\overset{+}{H} + \overline{IO_3} =$$

or $$2HI + \overline{IO_3} =$$

(ii) $$\bar{I} + \bar{I}_3 + 2\overset{+}{H} + \overline{IO_3} =$$

or $$HI + HI_3 + \overline{IO_3} =$$

in which the indices of the differential equations serve as coefficients.

The right-hand member of equation (i) may be filled in conjecturally thus,

$$2HI + \overline{IO_3} = 2HOI + \overline{IO},$$

giving HOI and its ion $\overline{OI}$ as the oxidation product of HI and reduction product of $\overline{IO_3}$ respectively. This assumption is in accordance with Roebuck's work on the reaction between arsenious acid and hydrogen iodide,[1] and with the current views on oxidation in organic chemistry, where the series of oxidation products of methyl alcohol, for instance, are regarded as derived from CH_4 by successive introduction of O between H and the electronegative element.

It is more difficult to invent a right-hand member for equation (ii); the following, however, might serve if it be supposed that the substance I_2OH (invented *ad hoc*) straightway decomposes into I_2 and IOH.

$$HI + HI_3 + \overline{IO_3} = HOI + HOI_2 + \overline{IO}.$$

My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose supervision it has been carried out.

The University of Toronto,
June, 1904.

[1] Jour. Phys. Chem. 6, 365 (1902).

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PAPERS FROM THE CHEMICAL LABORATORIES

No. 49: THE ELECTROLYSIS OF ACID SOLUTIONS OF ANILINE, BY LACHLAN GILCHRIST

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THE ELECTROLYSIS OF ACID SOLUTIONS OF ANILINE

BY LACHLAN GILCHRIST

When hydrochloric acid is electrolyzed, chlorine is set free at the anode, and it seemed quite feasible to dissolve a little aniline in the acid and let it be converted into chlor-aniline by the chlorine set free, just as the soda in the electrolysis of salt solutions is converted into hypochlorite.

Accordingly, a solution of 10 g of aniline, 50 cc of hydrochloric acid s. g. 1.2, and 50 cc water was made up, and a current of 30 amperes was passed through it, using pieces of platinum foil 2 x 5 cm as electrodes. It was not thought necessary to keep the aniline away from the cathode, as the chlor-aniline, once formed, is not easily reduced.

Formation of aniline black

In a few minutes, however, a greenish smudge appeared at the anode and soon spread through the liquid. As this was obviously due to the formation of "aniline black" (one of the oxidation products of aniline) and meant an impure product and a bad yield, the experiment was broken off.

It is well known that in the electrolysis of hydrochloric acid oxygen is often given off together with the chlorine, the proportion depending on the concentration of the acid and on the current density. It therefore seemed possible that by reducing the latter and increasing the former the chlorine evolved might be more nearly pure, and the formation of the oxidation product prevented.

The attempt was made in the next electrolysis, in which ½ amp was passed through a solution of 5 g of freshly distilled aniline in 100 cc of hydrochloric acid of s. g. 1.2; but aniline black was formed as before. Four other experiments carried out under different conditions of current density and concentration gave the same result. In Experiment 6 a little mannite

was added to the solution to prevent oxidation, but without effect.

TABLE I

No.	HCl s. g. 1.2	Aniline	Water	Current	Temp.
1	50 cc	10 g	50 cc	30 amp	18°–37°
2	100 cc	5 g	—	½ amp	18°–23°
3	100 cc	5 g	—	27 amp	30°–40°
4	100 cc	small amt	—	½ amp	25°
5	100 cc	small amt	—	1½ amp	24°–10° (in ice)
6	100 cc	10 g of HCl —aniline	10 cc	1½ amp	10° (in ice)

Determination of decomposition-voltage

The formation of aniline black in all these cases raised the question whether after all this substance might not be the primary product of the electrolysis; to test this point preparations were made to determine the decomposition-voltage of the solution.

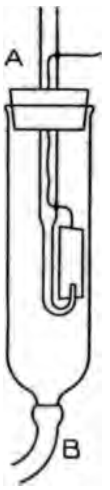

Fig. 1

The apparatus differed but slightly from that used by other investigators in measuring decomposition-voltages. The cathode cell is represented in Fig. 1, hydrogen was led in by A, and the connection with the anode compartment was effected through the narrow rubber tube B (25 cm long, 3 mm internal diameter.)

The first experiments were made with normal hydrochloric acid, and a good deal of trouble was experienced in obtaining accordant results. After a number of trials, however, it was found that:—

(i) Electrolytic hydrogen must be used in place of hydrogen from zinc and sulphuric acid.

(ii) The anode should be cleaned before each experiment, by treatment with hot nitric acid and water, then heated to red heat, then again washed with hot nitric acid, water, and alcohol, and dried in the air.

(iii) Changing the length of the anode wire from 2.5 mm to 1 mm has but little effect on the results.

(iv) Platinizing the anode wire has but little effect.

(v) Covering it with a glass tube, so as to reduce the volume of the anode compartment, has but little effect.

(vi) Shaking the anode has only a temporary effect; but the solution must not mix with the cathode solution.

(vii) The measurements should be taken with rising E. M. F. If taken in the opposite direction the cell must be short-circuited between measurements, and then at least ten minutes must be allowed for the galvanometer to reach a steady state.

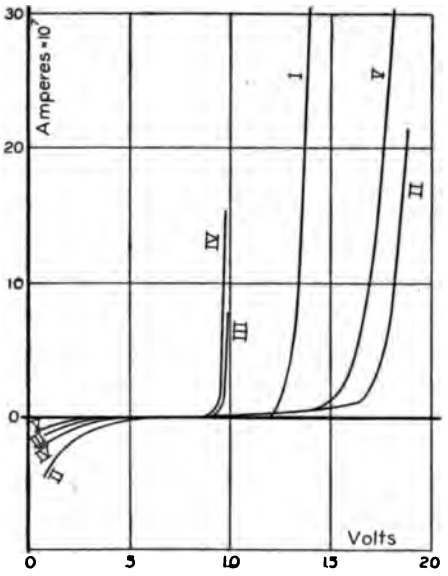

Fig. 2

If these points be attended to, fairly satisfactory measurements can be made; and the galvanometer comes to its final position within two to ten minutes from the time of changing the voltage.

The results of the work with hydrochloric acid are given in Table 2 and Curve I (Fig. 2). The curve rises suddenly at 1.25 volts; this is the well known "chlorine kink;" at lower voltages no chlorine is liberated from the solution. The result with

normal sulphuric acid is given in Table 3 and Curve II (page 541). The curve here rises suddenly at about 1.66 volts as is also well known.

TABLE 2

Normal Hydrochloric Acid

Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$
1.18	−0.2	1.308	+6.3
1.213	+0.6	1.33	8.0
1.241	1.2	1.35	10.5
1.265	2.8	1.38	21.2
1.288	4.2	1.4	41.5

TABLE 3

Normal Sulphuric Acid

Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$
0.036	4.25	0.58	−0.08	1.208	+0.127
0.148	3.66	0.638	0.04	1.23	0.151
0.172	3.08	0.668	0.03	1.272	0.191
0.21	2.72	0.743	0.005	1.307	0.218
0.25	1.37	0.84	+0.028	1.334	0.28
0.319	0.87	0.876	0.043	1.46	0.41
0.36	0.69	0.943	0.058	1.493	0.98
0.421	0.61	1.005	0.07	1.659	1.18
0.484	0.38	1.139	0.093	1.786	6.12
0.546	0.27	1.176	0.109	1.875	21.2

Aniline hydrochloride was then dissolved in the normal hydrochloric acid in the proportion of one-tenth molecule per liter, and the measurements repeated. It was quite impossible to obtain a steady reading on the galvanometer, as the current kept falling for several hours after the voltage was applied (see Table 4). The same is true of solutions of aniline in normal sulphuric acid (see Table 5).

In these experiments of long duration the formation of aniline black at the anode could be observed; that this was not due to oxidation by the air is shown by a blank experiment in which air was blown through the same solution in presence of a piece of platinum for 48 hours without causing the slightest turbidity or coloration.

TABLE 4

Normal Hydrochloric Acid and Tenth-Normal Aniline

Volts	Amperes $\times 10^7$	Time
2	−0.042	4 min.
4	−0.018	6 "
4	−0.02	4 hrs.
6	+0.002	6 min.
6	−0.009	16 hrs.
6	−0.008	5 "
8	+0.03	6 min.
8	−0.002	3 hrs.

TABLE 5

Normal Sulphuric Acid and Tenth-Normal Aniline

Volts	Amperes $\times 10^7$	Time
10	−0.34	4 min.
10	0.63	19 hrs.
15	0.12	4 "
19	0.62	10 min.
19	0.38	34 "
19	0.015	20 hrs.
22	2.72	50 min.
22	1.5	2 days
24	6.18	4 min.
24	3.67	1½ hrs.
24	3.3	½ hr.
27	10.0	7 min.
Dark greenish smudge commenced to form		
27	11.3	7½ min.
27	13.2	8 "
27	19.2	1 hr.
27	22.3	1 "

The cell was again filled with the aniline acid solution, hydrogen passed in at the large electrodes as before, the primary circuit broken at Y, and the current and E. M. F. determined. Both rose steadily until the current reached 1.4×10^{-7} amp and the E. M. F. V = 0.012 volt, after which the voltage fell, the current increased, and aniline black appeared in the anode solution.

From these experiments it is clear that a definite current for each voltage is not to be expected; the figures given in Table 6 and plotted in Curve III were therefore arbitrarily taken four minutes after adjusting the E. M. F. The sudden rise in the curve occurs at 0.95 volt, 0.30 volt below the chlorine kink. This shows that the aniline acts as a "depolarizer" in hydrochloric acid solution, but whether owing to the formation of a chlor-aniline, or of aniline black, does not appear.

TABLE 6

Normal Hydrochloric Acid and Tenth-Normal Aniline

Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$	Volts	Amperes $\times 10^7$
0.029	−1.7	0.432	−0.01	0.739	+0.01
0.099	1.33	0.472	0.002	0.784	0.01
0.19	0.54	0.485	0.000	0.84	0.014
0.264	0.21	0.535	+0.004	0.91	0.055
0.328	0.08	0.569	0.006	0.936	0.2
0.368	0.05	0.609	0.006	0.971	1.37
0.403	0.02	0.664	0.007	0.988	4.3

Decomposition voltages in sulphuric acid solutions

A set of measurements was then made under the same conditions as those of Table 4, but using normal sulphuric acid and one-tenth mol of aniline sulphate per liter, instead of the hydrochloric acid and the chloride. The results are contained in Table 7 and Curve IV.

Curve IV has its kink at the same voltage (0.95 volt) as Curve III for the experiments in which hydrochloric acid was used. The simplest explanation is that in both cases the same product is formed; in absence of hydrochloric acid this can not

be chlor-aniline; it must therefore be an oxidation product, presumably the aniline black.

With this difference of 0.30 volt in favor of the oxidation, it seems very unlikely that any chlorine could be liberated in hydrochloric acid to which aniline had been added. By increasing the current density at the anode sufficiently, however, it might be possible to oxidize the aniline at that electrode more quickly than it could be replaced by convection or diffusion; so that, for part of the time, the solution would consist of pure hydrochloric acid, and chlorine would be liberated. At best the yield of chlor-anilines would be low, and the product impure.

TABLE 7

Normal Sulphuric Acid and Tenth-Normal Aniline

Volts	Amperes × 10^7	Volts	Amperes × 10^7
0.029	−2.7	0.667	−0.015
0.111	1.48	0.711	0.002
0.21	1.06	0.742	+0.002
0.273	0.75	0.778	0.008
0.341	0.5	0.814	0.012
0.374	0.347	0.847	0.02
0.406	0.25	0.872	0.042
0.438	0.19	0.909	0.145
0.479	0.132	0.941	0.8
0.506	0.125	0.956	2.5
0.538	0.072	0.969	7.45
0.577	0.039	0.948	15.5
0.604	0.023	Aniline black commenced to form before last reading was made	

These conclusions are in agreement with the results of an experiment in which 100 grams of aniline were dissolved in 450 cc of hydrochloric acid of s. g. 1.2, and electrolyzed with a current of 7.5 amperes for 7¾ hours. The anode was a piece of arc light carbon 11 cm long; the cathode platinum 2 x 5 cm. No chlorine was noticed in the gases given off. The vessel containing the electrolyte was surrounded by an ice-bath, but the temperature rose to 38° C.

After the electrolysis the dark liquid was filtered and

evaporated. On cooling, 50 grams of crystals were deposited, and three days later another crop of fourteen grams was obtained. These crystals, and the final mother-liquor were examined for chlor-aniline by adding caustic soda in excess, extracting with ether, removing the ether on a water-bath, and fractionating the residual oil. The boiling-point rose rapidly to 179°, and all but 4 or 5 cc passed over at 179°–181°, the boiling-point of aniline. The residue contained a little chlorine; thus while chlor-anilines are formed, they amount to but a few percent of the weight of the aniline employed.

Aniline and hydrobromic acid

As the oxidation potential of aniline (0.95 volt) lies above the decomposition voltage of hydrobromic acid (0.75 volt in 4-*n* HBr), it follows that on electrolysis of a solution of aniline in hydrobromic acid bromine will be liberated, and aniline black will not be formed. This conclusion is confirmed by the following experiment.

25 g of potassium bromide, 12.5 cc of pure sulphuric acid, and 0.9 g of aniline were dissolved in water, the total volume of the solution being 65 cc; a precipitate of potassium sulphate was removed by decantation.

TABLE 8

n-Sulphuric Acid, *n*/10 *m*-Nitraniline

Volts	Amperes × 10^7	Volts	Amperes × 10^7
0.20	−1.20	1.56	+3.3
0.21	0.27	1.59	4.0
0.27	0.17	1.62	6.8
0.31	0.11	1.65	9.0
0.41	0.02	1.69	12.0
0.75	+0.08	1.73	15.32
0.96	0.22	1.75	18.1
1.27	0.30	1.76	20.4
1.47	0.78	1.79	26.0
1.53	1.82	1.81	29.0

A current of 0.25 ampere was passed through this solution between platinum electrodes (anode 2 x 5 cm, cathode 2 x 1 cm)

for ten minutes. No aniline black was formed, but the anode became covered with a deposit of white matted crystals, stained with bromine. These crystals were removed, washed, and dried and their melting-point found to be 116° ; *s*-tribrom-aniline melts at 118°.

m-Nitraniline

From chemical considerations it seemed probable that nitraniline would be less easily oxidized than aniline itself. To test this view, a series of experiments analogous to those of Curve IV were undertaken, in which *m*-nitraniline, instead of aniline was dissolved in the sulphuric acid.

The results are plotted in Curve V. The oxidation potential of *m*-nitraniline lies at 1.43 volts, 0.2 above the chlorine kink.

Summary

The conditions under which decomposition-voltages can be determined in acid solutions of aniline are specified (page 541).

The formation of aniline black from *n*/10 aniline in solutions of *n*-hydrochloric acid or *n*-sulphuric acid takes place at 0.95 volt (small anode, hydrogen cathode).

Therefore only traces of chlor-aniline are formed on electrolysis of aniline in hydrochloric acid solution; but brom-anilines are formed by the electrolysis of solutions containing hydrobromic acid and aniline. The aniline solutions thus resemble those of phenol.[1]

The oxidation potential of *m*-nitraniline in sulphuric acid solution (1.43 volts), is much higher than that of aniline.

My thanks are due to Prof. W. Lash Miller, at whose suggestion these measurements were carried out.

University of Toronto,
June, 1904

[1] Zehrlant. Zeit. f. Elektrochem. 7, 501 (1901).

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SOME COMPOUNDS OF CHROMIC CHLORIDE WITH SUBSTITUTED AMMONIAS.

BY W. R. LANG AND C. M. CARSON.

Received April 18, 1904.

IT HAS already been shown that dry liquid ammonia forms with violet chromic chloride a pink powder which, when extracted with water, gives crystalline compounds containing 12, 10 and 8 molecules of ammonia respectively.[1] In addition to this, compounds with methylamine were also obtained and described in a previous paper.[2] The authors have made a series of experiments with other substituted ammonias, the results of which are as follows:

(1) *Ethylamine,* $C_2H_5NH_2$, acts on the chloride with great energy at temperatures between 0° and 18°, producing a dark red powder. On extracting this compound with water and evaporating carefully, red crystals are obtained which, on analysis, give:

	Per cent.
Chromium	12.97
Chlorine	26.38
Ethylamine	55.90
Water	4.75

corresponding thus to the formula $Cr_2Cl_6.10C_2H_5.NH_2 2H_2O$.

When the red powder is heated to 60° and again extracted with water, the solution yields crystals composed of

	Per cent.
Chromium	14.53
Chlorine	29.85
Ethylamine	50.40
Water	5.22

indicating the existence of the compound $Cr_2Cl_6.8C_2H_5.NH_2 2H_2O$.

(2) *Dimethylamine and Diethylamine* do not react with chromic chloride at any temperature between zero and their boiling-points. If moisture be present, however, chromic hydroxide forms on standing for a few hours.

(3) *Trimethylamine and Triethylamine,* like the secondary amines, have no effect on chromic chloride.

[1] Lang and Carson: This Journal, April, 1904, pp. 414-417.
[2] Lang and Jolliffe: *Ibid.*, p. 417.

(4) *Ethylene Diamine* reacts violently with the chloride at temperatures between zero and 18° with the evolution of a large amount of heat and the production of a dark red powder. This, when dissolved in water and evaporated in the air, yields dark red crystals having the composition:

	Per cent.
Chromium	12.43
Chlorine	12.40
Ethylene diamine	57.50
Water	4.67

The formula of this substance is thus $Cr_2Cl_6.8C_2H_4(NH_2)_2.2H_2O$.

(5) *Aniline, Methylaniline, and Dimethylaniline* do not have any action whatever on chromic chloride either at zero or at the boiling-points of the liquids, even when maintained in contact for a considerable time.

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No. 52: TRIBROMPHENOLBROMIDE, ITS DETECTION, ESTIMATION, RATE OF FORMATION, AND REACTION WITH HYDRIODIC ACID, BY S. J. LLOYD

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THE DETERMINATION OF PHENOL.

BY S. J. LLOYD.

Received October 27, 1904.

NUMEROUS attempts have been made to devise a satisfactory method for the quantitative estimation of phenol.

Beckurts[1] mixed the phenol with its own volume of petroleum spirit, shook with a strong solution of caustic soda in a graduated tube, and noted the change in volume; Bader[2] titrated against a decinormal solution of sodium hydroxide with symmetrical trinitrobenzene as indicator;[3] Messinger and Vortmann[4] precipitated the triiodo derivative with an alkaline solution of iodine; Carré[5] treated the phenol with nitric acid and determined the resulting picric acid colorimetrically; Schaedler[6] used sulphuric acid, and determined the phenolsulphonic acid indirectly with barium; Riegler[7] weighed the precipitate with *p*-diazonitraniline; Toscher[8] oxidized with volumetric permanganate in boiling alkaline solution; while the reaction with sodamide has been applied by Schryver[9] to the determination of the "hydroxyl value" of phenol.

Of these methods, the first evidently makes no pretense to accuracy, and indeed, like the sulphonic acid process, is intended for use with crude phenol only. Titration with soda is not possible with solutions containing less than 2 per cent. of phenol,[10] and in any case the end-point is not sharp. Precipitation with iodine requires careful manipulation and exact regulation of the temperature in order to obtain accurate results;[11] the colorimetric method is unsuited to the determination of phenol in other than very small quantities, the reaction with the diazo compound leads to a tedious gravimetric process, and the sodamide method requires special apparatus, and can be used only with perfectly dry phenol.

The reaction of phenol, however, which is best suited for the

[1] *J. Soc. Chem. Ind.*, **5**, 546 (1886) (from *Arch. Pharm.*, **24**, 567 (1886)).

[2] *Ztschr. anal. Chem.*, **31**, 58 (1892).

[3] For the behavior of phenol with other indicators, see Imbert and Astruc: *Compt. Rend.*, **130**, 35 (1900).

[4] *Pharm. Ztg.*, **29**, 759.

[5] *Compt. Rend.*, **113**, 139 (1891).

[6] *Centrbl.*, 1872, p. 506 (from *Pharm. Centrbl.*, **13**, 225).

[7] *Centrbl.*, 1899, II, p. 322 (from *Buletinul din Bucuresci*).

[8] Meyer's *Jahrbuch, d. Chemie*, 1901, p. 253 (from *Pharm. J.*, 1901, No. 1602).

[9] *J. Soc. Chem. Ind.*, **18**, 553 (1899).

[10] Frerichs: *Centrbl.*, 1896, II, p. 2141 (from *Apoth. Ztg.*, **11**, 415).

[11] Frerichs: *Loc. cit.*

purposes of quantitative determination, is that with bromine,

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

Landolt,[1] who was the first to suggest its use, precipitated the tribromphenol with bromine water, dried in a desiccator and weighed; Chabrie[2] extracted with ether and dried in a special apparatus. Koppeschaar[3] shortened the process by using a measured quantity of bromine water, and titrating back the excess with potassium iodide and sodium thiosulphate; he also found it advisable to replace the unstable and disagreeable bromine water by a mixture of potassium bromide and bromate, from which the bromine was liberated at the proper time by acid. Degener,[4] who was apparently unacquainted with Koppeschaar's work, also used bromine water, but determined the end-point by the disappearance of the yellow color of the solution, or by potassium-iodide-starch paper. Chandelon[5] found the time required for an analysis by the Koppeschaar method too long, and in order to shorten it and avoid loss of bromine as vapor and as a mechanical enclosure in the precipitate, he substituted for the bromide-bromate mixture a hypobromite solution which contained sufficient alkali to hold the tribromphenol in solution. The disappearance of the yellow color of the solution, or the failure to discolor potassium-iodide-starch paper, marked the end of the reaction. Telle[6] used volumetric sodium hypochlorite, which he added to the solution of phenol containing excess of potassium bromide, and determined the end-point by the color of the solution. Waller's[7] method differed from that of Degener only in the addition of a saturated solution of alum to make the precipitate more dense. Seubert[8] followed Koppeschaar in liberating the bromine from a bromide-bromate mixture, and added the phenol solution from a burette until the filtrate gave no further color with potassium-iodide-starch paper, while Beckurts[9] used an excess of the bromide-bromate mixture, and titrated back with iodide and thiosulphate. The last-named chemist recognized the presence of tribromphenolbromide

[1] *Ber. d. chem. Ges.*, 4, 770 (1871).
[2] *Centrbl.*, 1898, 1, 1309 (from *Rev. Chim. Anal. Appl.*, 6, 138 (1898)).
[3] *Ztschr. anal. Chem.*, 15, 233 (1876).
[4] *J. prakt. Chem.*, N. F., 17, 390 (1878).
[5] *Bull. Soc. Chim.*, 38, 69 (1882).
[6] *Chem. News.*, 83, 51 (1901).
[7] *Ibid.*, 43, 152 (1881).
[8] *Ber. d. chem. Ges.*, 14, 1581 (1881), (from *Arch. Pharm.*, 18, 321).
[9] *J. Soc. Chem. Ind.*, 5, 546 (1886) (from *Arch. Pharm.*, 24, 561 (1886)).

in the precipitate, but assumed that it was quantitatively converted into tribromphenol by potassium iodide.

The following table may serve as a synopsis:

Gravimetric:

(1) Landolt, Chabrié.

Volumetric:

(2) *Bromine and phenol in acid solution.*

(*a*) End-point determined by color, or by potassium-iodide-starch paper.

Degener—Bromine water.
Telle —Hypochlorite and potassium bromide.
Waller —Bromine water and alum.
Seubert —Bromide-bromate mixture.

(*b*) Excess bromine determined by potassium iodide.

Koppeschaar—Bromine water or bromide-bromate mixture.
Beckurts—Bromide-bromate mixture.

(3) *Bromine and phenol in alkaline solution.*

Chandelon.

Various modifications for use in the estimation of phenol in tar-oil, urine, soaps, etc., have been suggested by Tóth,[1] Kleinert,[2] Fedeli,[3] Giacosa,[4] Endemann, Neuberg,[5] Kossler and Penny,[6] Partheil,[7] Ditz and Cedivoda,[8] Stockmeier and Thurnauer[9] (who used chloroform in the titration), and others.

Some idea of the accuracy of the results obtainable by these different methods of procedure may be gleaned from the test analyses published by their authors. Landolt's numbers show variations of 0.5 per cent. or more, Koppeschaar's (bromine water) 2.5 per cent. (bromide-bromate) 0.5 per cent., Degener's 3 per cent., Chandelon 2 per cent., Seubert's 1.5 to 3 per cent. No test analyses have been published by Waller or Telle. According to Frerichs,[10] Beckurt's modification is the best, but as his paper, in its original form, is not accessible to me, I am unable to quote the results of this author's analyses.

These discrepancies are due, in part at least, to the formation

[1] *Ztschr. anal. Chem.*, **25**, 160 (1886).
[2] *Ibid.*, **23**, 1 (1884).
[3] *Ber. d. chem. Ges.*, **28**, 1060 R (1895), (from Moleschott's *Untersuchung.*, **15**, 583).
[4] *Ztschr. physiol. Chem.*, **6**, 43 (1878).
[5] *Ibid.*, **27**, 123 (1899).
[6] *Ibid.*, **17**, 117 (1889).
[7] Meyer's *Jahrbuch d. Chemie*, 1896, p. 237 (from *Apoth. Ztg.*, 1896).
[8] *Ztschr. angew. Chem.*, 1899, pp. 873 and 897.
[9] Mohr: *Titrirmethode*, 7th ed., p. 386 (1896) from *Chem. Ztg.*, 1893, pp. 113 and 1[illegible].
[10] *Centrbl.*, 1896 (II), 2141.

of tribromphenolbromide, which, as I have shown in a previous paper,[1] is produced by the action of bromine water on the precipitated tribromphenol, and once formed is not quantitatively reconverted into tribromphenol by potassium iodide.

The present paper, after dealing with the loss of bromine by evaporation during the analysis, the use of volumetric solutions containing bromates, and the formation of a new product of the action of bromine on phenol, contains the results of a number of test-analyses in which the precautions suggested by the previous experiments were adopted, and closes with an enumeration of the conditions under which phenol may be accurately determined.

SOLUTIONS EMPLOYED.

Phenol.—Merck's "absolute phenol" was distilled three times, the first and last fractions being rejected in each case, and the portions boiling between 182° and 183° collected. In the last fractionation the distillate was received in a tared and stoppered weighing-glass, cooled, weighed (20.5340 grams) and dissolved to 1 liter. The solution used in the following analyses was made by diluting 100 cc. of this solution to 1 liter.

Hypobromite.—About 9 cc. of bromine were dissolved in 2 liters of N/4 caustic potash, and the solution was standardized by adding potassium iodide and hydrochloric acid, and determining the iodine with decinormal thiosulphate.

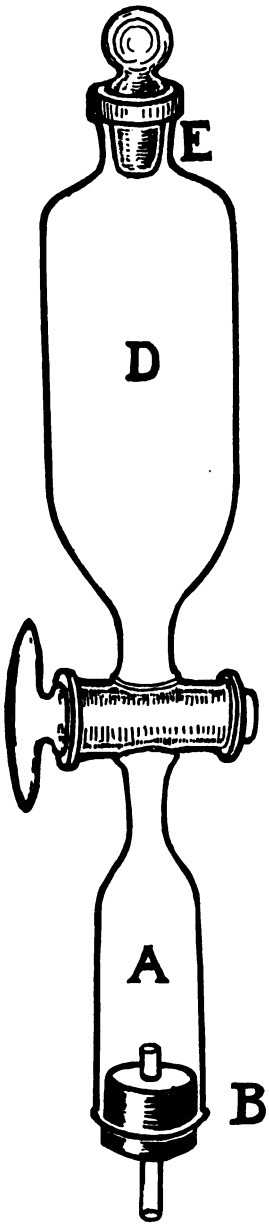
One hundred cc. of the phenol solution were equivalent to 71.95 cc. of the hypobromite.

Sodium Thiosulphate.—One liter of an approximately N/10 solution was prepared and standardized with iodine which had been ground with potassium iodide, sublimed from the mixture, and dried for three days in a vacuum desiccator over sulphuric acid. The value was found to be 0.1045 N. This solution was used to fix the titre of the alkaline solution of bromine as stated above, and in turn was repeatedly standardized against the latter solution; it showed a slight falling off in normality from 0.1045 to 0.1042 in two weeks.

For use in the phenol determination the decinormal thiosulphate was diluted to five times its volume and the ratio controlled by comparison with an iodine solution.

Iodine, approximately N/50 for use in "titrating back."

[1] This Journal, 27, 7 (1905).



Acid, hydrochloric, "strictly chemically pure" (sp. gr. 1.2).

Potassium Iodide, 17 grams in 100 cc.

The solutions were prepared and standardized with every care, the burettes were calibrated before using, and a special burette reader was employed, by means of which hundredths of a cubic centimeter could readily be distinguished.

LOSS OF BROMINE BY EVAPORATION.

The test analyses published at the close of this paper were carried out in a 0.25 liter long-necked glass-stoppered measuring flask. In order to assure myself that there was no loss of bromine by evaporation, two measurements were made in the apparatus sketched in the accompanying figure (made by sealing an adapter to a separating funnel).

The chamber *A* was closed by the perforated rubber stopper *B*, the tap opened and the whole exhausted with a filter-pump; the tap was then closed, *B* removed, and the apparatus fixed in a stand, *A* upwards. Fourteen cc. of the hypobromite (or bromide-bromate solution) were then pipetted into *A* and sucked into *D* by slightly opening the tap; this was followed by 25 cc. of acid and then 20 cc. of phenol solution; the vessel *A* was rinsed out with 10 cc. of water between each addition and the rinsings sucked into *D*. After shaking and allowing to stand for five minutes, 5 cc. of the potassium iodide solution were added in the same manner; the tap was then opened to restore atmospheric pressure in *D* and the contents poured through *E* into a beaker containing 150 cc. of water, where

the iodine was titrated by sodium thiosulphate. From the thiosulphate required the excess of bromine was calculated, and by subtracting from the original 14 cc. the "KOBr used" of the table was obtained.

Experiments identical in every respect, except that the 250 cc. flask was used instead of the apparatus just described, were carried out at the same time; as is shown in Table I, the results differ only by one or two parts per thousand. It is thus proved that the operation may be carried out in a flask without loss of bromine. Some care, however, is necessary; in one case where the bromine vapor was purposely blown out of the flask, an error of 2 per cent. in the analysis resulted.

TABLE I.

Hypobromite, 14 cc.; acid, 25 cc.; water, 30 cc.; phenol, 20 cc.; iodide, 5 cc.; time, five minutes.

Hypobromite.	Apparatus.	KOBr used.	Differences.
Fresh	Flask	13.91	0.0
Fresh	See figure	13.91	
Evaporated	Flask	13.96	0.02
Evaporated	See figure	13.94	

ACTION OF BROMIC ACID ON PHENOL AND THE USE OF THE BROMIDE-BROMATE MIXTURE.

If a little potassium bromate be mixed with a solution of phenol and acid be added, the solution turns red and a red precipitate is deposited which contains bromine and does not liberate iodine with hydriodic acid. It is obvious that the formation of this substance, during the determination of phenol, would vitiate the result.

As old solutions of potassium hypobromite are liable to contain bromate, two pairs of experiments were undertaken to see whether errors could be introduced into the analysis from this source; in one of each pair 14 cc. of fresh hypobromite solution were used and in the other a solution of bromide and bromate made by evaporating 14 cc. of the same hypobromite to dryness and dissolving the residue. In one experiment of each of the pairs the reagents were mixed in the order *A*, hypobromite (or bromide-bromate mixture), acid, phenol, and in the other in the order *B*, acid, phenol, hypobromite (or bromide-bromate). The results with the bromide-bromate mixture were 3 or 4 parts per thousand higher than the others, while the order of mixing made no difference (see Table II). It is thus clear that the presence of a little bromate

in the hypobromite solution can exert no influence whatever on the result.

TABLE II.

Hypobromite, 14 cc.; acid, 25 cc ; water, 30 cc.; phenol, 20 cc.; iodide, 5 cc.; time, five minutes.

Hypobromite.	Order of mixing.	KOBr used.
Fresh	*A*	13.91
Fresh	*B*	13.94
Evaporated	*A*	13.96
Evaporated	*B*	13.96

NEW PRODUCT OF THE ACTION OF BROMINE ON PHENOL.

If solutions of phenol and potassium hypobromite be mixed and the mixture be acidified, the precipitated tribromphenol is mixed with a red powder. What seems to be the same compound was obtained as a by-product in the preparation of tribromphenolbromide, and by the action of alkaline solutions of bromine on tribromphenol. It melts at about 91° C. and contains about 64 per cent. of bromine, but does not liberate iodine with an acid solution of potassium iodide. It is insoluble in water, alcohol, ether, and in glacial acetic acid; soluble in carbon bisulphide, chloroform and benzene, giving red solutions. Its molecular weight in chloroform solution (boiling-point determinations) is 508 to 514. On warming with a 10 per cent solution of caustic potash, or with concentrated sulphuric acid, it is apparently unaltered, but by heating to a temperature above its melting-point it is converted into a substance resembling hexabromphenoquinone.

I propose, if possible, to determine the constitution of this substance. Its formation during an analysis would, obviously, introduce errors into the result, hence the analytical method of group 3 (page 18) cannot be recommended.

THE DETERMINATION OF PHENOL.

Four of the most likely sources of error in the present methods of determining phenol by bromine having been studied in detail, it remained to inquire whether determinations carried out under the conditions suggested by the foregoing experiments, would give accurate results. The test-analyses undertaken with the object of deciding this question were made in acid solution in order to avoid the formation of tribromphenolbromide;[1] they were carried out at room temperature in a long-necked, glass-stoppered 0.25-liter flask (page 20), and the bromine was introduced in the convenient form of a solution in caustic potash (page 22). The

[1] This Journal, 27, 7 (1905).

phenol solution was run into the flask from a burette, the acid added, and then the hypobromite from a pipette. The flask was closed, shaken for thirty seconds, and allowed to stand for the time given in the table after "t." Five cc. of potassium iodide solution were then added, followed by 100 cc. of water, and in some cases 10 cc. of chloroform. The whole was shaken for fifteen seconds, allowed to stand for two minutes, and the iodine determined with the N/50 thiosulphate.

TABLE III.

Hypobromite, 25 cc.; acid, 15 cc.

		10 cc. chloroform.		No chloroform.		
Phenol. cc.	Excess Br. cc.	$t = 0$. Per cent.	$t = 2$ minutes. Per cent.	$t = 0$. Per cent.	$t = 2$ minutes. Per cent.	$t = 5$ minutes. Per cent.
5	21.40	....	114.0	105.6	105.6	106.2
10	17.80	....	109.6	103.9	103.7	103.9
15	14.21	....	100.10	....	....	....
20	10.61	100.0	99.95	....	99.97	100.11
20	10.61	....	....	....	101.51*	102.71*
20	10.61	....	....	....	....	101.92†
25	7.01	....	100.05	99.62	99.83	99.83
25	7.01	....	....	....	100.35*	....
25	7.01	....	....	....	99.85	....
30	3.42	99.9	99.95	99.56	97.7	99.83
30	3.42	....	....	99.6	99.65	99.85
31	2.70	99.8	99.8	99.44	99.55	99.97
32	1.98	....	99.85	99.25	99.35	99.97
33	1.26	....	98.99	98.7	99.35	99.7
34	0.54	....	98.62	98.1	98.9	99.42
35	0.18	....	97.63	96.9	....	98.74

Under "Excess Br" is given the difference between the volume of the hypobromite employed, *viz.*, 25 cc. and the volume equivalent to the phenol taken (volume of phenol solution multiplied by 0.7195, see page 19). The results of the determinations are expressed as percentages of the amount of phenol actually present.

In the experiments marked with a star (*), 10 cc. of carbon bisulphide were used instead of chloroform, and in that marked dagger (†), 5 cc. of acid were used instead of 15 cc. In this experiment the precipitate, dissolved in chloroform, gave a distinct green with benzidine solution, indicating the presence of tribromphenolbromide.

Table IV contains the results of a few measurements in which sulphuric acid was used instead of hydrochloric. It is obvious that Koppeschaar[1] was mistaken in saying that the presence of sulphuric acid spoils the titration.

[1] *Zischr. anal. Chem.*, 18, 237 and 240.

TABLE IV.

Hypobromite, 25 cc.; sulphuric acid (sp. gr. 1.84), 11 cc.; chloroform, 10 cc.

Phenol. cc.	Excess Br. cc.	$t = 2$. Per cent.
20	10.61	99.91
25	7.01	99.85
30	3.42	100.11

The above experiments lead to the following:

DIRECTIONS FOR THE DETERMINATION OF PHENOL BY BROMINE.

The following solutions are needed.—Fiftieth-normal thiosulphate and iodine; starch; hydrochloric acid (sp. gr. 1.2); potassium iodide, 17 grams in 100 cc.; hyprobromite, prepared by dissolving 9 cc. of bromine in 2 liters of a solution containing 28 grams of caustic potash. The hypobromite must be compared with the thiosulphate by adding acid and potassium iodide and titrating the iodine set free.

To carry out the analysis.—Introduce the phenol solution into a glass-stoppered flask and add a volume of acid equal to about one-third or one-fourth of the combined volumes of the phenol solution and the hypobromite that will probably be added during the analysis.

Run in the hypobromite from a burette, shaking the flask, until the solution becomes permanently yellow. Then add an excess of the hypobromite (10 to 20 per cent. of that used already) and shake well. Finally add an excess of potassium iodide, dilute with water, add 10 cc. of chloroform, and determine the iodine with the volumetric thiosulphate. The object of diluting is to prevent the acid from acting on the potassium iodide or on the thiosulphate; if 10 cc. of water be added at this stage for every cubic centimeter of acid previously added, the solution will be sufficiently dilute. The use of chloroform may be dispensed with, if the mixture be allowed to stand five minutes before adding the potassium iodide; it is, however, better to use the chloroform,—carbon bisulphide is not satisfactory.

If these directions be adhered to, the phenol can be determined within 1 or 2 parts per thousand.

In conclusion, the author wishes to express his thanks to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

THE UNIVERSITY OF TORONTO,
March, 1904.

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TRIBROMPHENOLBROMIDE: ITS DETECTION, ESTIMATION, RATE OF FORMATION, AND REACTION WITH HYDRIODIC ACID.

By S. J. Lloyd.

Received October 27, 1904.

The following experiments form part of an investigation of the reaction between bromine and phenol, which was undertaken with the object of improving Koppeschaar's method of determining the latter substance.

The tribromphenolbromide used was prepared by Werner's[1] recipe, recrystallized three times from chloroform, and dried for three days over sulphuric acid in a vacuum; it formed golden-yellow crystals, melting-point 119°.

DETECTION.

When searching for a distinctive qualitative test for tribromphenolbromide, I found that ammonia, and chloroform solutions of many of the organic bases react with it to form colored products, as follows:

[1] *Bull. Soc. Chim.*, **43**, 372 (1885).

Ammonia	Brown.
Aniline	Deep red, turning muddy.
Dimethylaniline	Slight darkening.
Paratoluidine	Clear red
Diphenylamine	Light red.
α-Naphthylamine	Dark blue, turning purple.
β-Naphthylamine	Light rose-pink, appears very slowly.
Aminoazobenzene	Brown-red, appears very slowly and gradually deepens.
Pyridine	Light yellow.
Benzidine	Intense green, purple if concentrated.

Azoxybenzene, Metanitraniline, Acetanilide, no change.

Of these, aniline and benzidine proved most suitable as reagents; with tribromphenol, tetrabromphenol and hexabromphenoquinone they give no color, while with bromine water an aniline solution is bleached, and benzidine gives a seal-brown, quite distinct from the green with tribromphenolbromide.

The benzidine solution may be prepared by warming 5 grams of benzidine sulphate with 50 cc. of a 10 per cent. potash solution, cooling, extracting the benzidine with chloroform, and filtering off the chloroform solution. Three drops of this reagent give a distinct green with 10 cc. of a solution containing 1 gram of tribromphenolbromide in a liter of chloroform. Shaking the tribromphenolbromide solution with decinormal sodium thiosulphate before adding the benzidine reagent does not interfere with the color reaction.

ESTIMATION.

As the reaction with potassium iodide is obviously unsuitable (see page 20), a basis for the method was sought in the action of reducing agents; Benedict[1] states that zinc and hydrochloric acid reduce tribromphenolbromide to tribromphenol, but does not seem to have made any quantitative measurements. After experimenting with sodium amalgam and with magnesium, I finally decided in favor of powdered zinc and sulphuric acid, which are without action upon tribromphenol, but remove one atom of bromine from tribromphenolbromide. By determining the bromine in the solution after reduction, it is thus possible to calculate the amount of tribromphenolbromide in the substance analyzed. The details of the method are as follows:

The tribromphenolbromide was placed in a 150 cc. flask, 20 cc.

[1] *Ann. Chem.* (Liebig), **199**, 127 (1879).

of alcohol (96 per cent.), 5 cc. N/4 sulphuric acid and about 0.25 gram powdered zinc[1] were added, and the flask heated on a water-bath until the whole of the tribromphenolbromide had dissolved and the solution had lost its characteristic yellow color. Excess of calcium carbonate was then added to neutralize the free sulphuric acid, and the alcohol together with most of the tribromphenol were distilled off on a water-bath; the residue was extracted with three successive portions of boiling water, 25 cc., 25 cc., and 10 cc., respectively; and in the filtrate, after cooling, the bromine was determined by N/10 silver nitrate with potassium chromate as indicator. Blank experiments with tribromphenol showed that no bromine was removed by this treatment.

TEST ANALYSES.

Tribromphenolbromide. Gram.	$AgNO_3$ found. cc.	$AgNO_3$ calc. cc.	Per cent.
0.5023	12.45	12.46	99.92
0.5327	13.19	13.11	100.61
0.5249	12.80	12.92	99.07

NOT THE PRIMARY PRODUCT.

The precipitate formed by the action of bromine water upon phenol is at first pure white in color, but on standing with the solution containing excess of bromine it gradually assumes a yellowish tint; the change is due to the formation of tribromphenolbromide, the presence of which was detected by the qualitative tests described above. The change of color shows that tribromphenolbromide is not the primary product of the action of bromine water upon phenol, as imagined by Weinreb and Bondi,[2] but is formed by a gradual reaction between the precipitated tribromphenol and the excess of bromine.

RATE OF FORMATION.

By means of the method of analysis described above, the amount of tribromphenolbromide formed when the phenol was treated with bromine under varying conditions was determined.

The following solutions were employed: *Phenol,* 20 grams per liter; *silver nitrate,* 16.83 grams per liter; the tribromphenolbromide from 5 cc. of the phenol solution is thus equivalent to 10.74 cc. of the silver nitrate. *Hypobromite,* bromine was dissolved in a solu-

[1] This is more than enough, excess does no harm.

[2] *Monatshefte f. Chemie,* 6, 506 (1885).

tion of caustic potash of known alkalinity (about quarter normal) and a solution of *hydrochloric acid* equivalent to the potash was prepared, so that on mixing the alkaline solution of bromine with an equal volume of the equivalent acid a neutral bromine solution resulted. By titration with volumetric sodium thiosulphate after adding acid and potassium iodide, 50 cc. of the hypobromite solution were found to contain 0.6810 gram bromine; hence to convert 5 cc. of the phenol solution into tribromphenol requires 37.45 cc. of the hypobromite solution; to convert it into tribromphenolbromide requires 49.94 cc. Allen[1] states that hypobromite solutions prepared like that above, and containing a large excess of alkali do not appreciably alter their content of available bromine upon standing or heating.

The experiments were carried out as follows: 50 cc. of the hypobromite solution were pipetted into a glass-stoppered quarter-liter measuring flask, then 50 cc. of the equivalent acid added and finally 5 cc. of the phenol solution. The mixture was shaken for thirty seconds and allowed to stand for a measured interval, after which the mother-liquor was rapidly removed by means of a filter-pump and a large perforated porcelain funnel. The precipitate was washed with cold water until the addition of silver nitrate produced no cloudiness in the filtrate, and was then brought, filter-paper and all, into a 150 cc. flask, where the tribromphenolbromide was determined as described above.

In some of the experiments the concentration of the bromine was altered by adding bromine from a burette; in others, previous to the addition of phenol, the solution was acidified with hydrochloric acid (sp. gr. 1.2), while in others weighed quantities of potassium bromide were added. The results are contained in Tables I to VI.

The effect of varying the time during which the bromine water acted upon the tribromphenol, *i, e.*, the interval between adding the phenol and filtering, was first studied. The results of these experiments are contained in Table I; they afford ample proof that the tribromphenolbromide is a secondary product and show what a large amount of it may be formed in a few minutes under the ordinary conditions of a phenol determination.

[1] *J. Soc. Chem. Ind.*, **3**, 65 (1884).

TABLE I.—EFFECT OF TIME.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Time. Minutes.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
5	2.36	22
10	4.11	38
15	5.13	48
30	7.49	70
Hours.		
18	7.75	72

Under $AgNO_3$ is given the volume of the silver nitrate solution required in the analysis; the numbers under "Tribromphenolbromide" (obtained by dividing the figures in the second column by 10.74) represent the fraction of the phenol which has been converted into tribromphenolbromide.

The experiments of Tables II, III, IV, V and VI show that the amount of tribromphenolbromide formed from 5 cc. of the phenol solution in a constant interval (five minutes) increases with the excess of bromine and with the volume of the reacting mixture, and is diminished by adding acid or potassium bromide, or by lowering the temperature. They afford a striking parallel to the results obtained by Mr. Roebuck in his study of the rate of oxidation of arsenious acid by iodine,[1] where the rate is proportional to the concentration of the iodine and to the volume of the solution, and inversely proportional to the concentration of the acid and of the potassium iodide; Roebuck interpreted his results by assuming that hypoiodous acid is the oxidizing agent in iodine solutions; a similar explanation of my own experiments, *viz.*, that the formation of tribromphenolbromide from tribromphenol is due to the oxidizing action of hypobromous acid, naturally suggests itself.

TABLE II.—EFFECT OF VOLUME.

KOBr, 50 cc.; equiv. HCl, none;* HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Volume. cc.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
57	1.19	11
106	2.36	22
157	3.84	36
207	4.6	43

* To keep down the volume. The 1 cc. of strong hydrochloric acid was very slightly more than enough to neutralize the alkali of the hypobromite solution.

[1] *J. Phys. Chem.*, 6, 365 (1902).

TABLE III.—EFFECT OF BROMINE.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total excess bromine. Grams.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
0.17	2.36	22
0.55	5.59	52
0.92	7.02	66
1.67	8.74	81

TABLE IV.—EFFECT OF ACID.

KOBr, 50 cc.; equiv. HCl, 50 cc.; phenol, 5 cc.

Total acid. Mol.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
0.016	2.36	22
0.029	2.78	17
0.068	1.37	13
0.068	1.35	13
0.133	0.35	3
0.198	0.1	1

TABLE V.—EFFECT OF POTASSIUM BROMIDE.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Total KBr. Mol.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
0.003	2.36	22
0.0073	1.69	15.7
0.0116	0.51	4.7
0.0288	0.25	2.3
0.0546	0.23	2.2

TABLE VI.—EFFECT OF TEMPERATURE.

KOBr, 50 cc.; equiv. HCl, 50 cc.; HCl (sp. gr. 1.2), 1 cc.; phenol, 5 cc.

Temperature. °C.	$AgNO_3$. cc.	Tribromphenolbromide. Per cent.
0	1.9	18
18	2.36	22

These experiments show clearly that in order to avoid the formation of tribromphenolbromide when titrating phenol with bromine, the liquid must be strongly acid or must contain an excess of potassium bromide: the excess of bromine must not be too great, and the time during which the precipitate of tribromphenol is in contact with the excess of bromine must not be too long. Under these conditions only a mere trace of tribromphenolbromide is formed, and it is precisely when the quantity of that substance is smallest that it is most easily acted upon by hydriodic acid (see Table VII).

REACTION WITH HYDRIODIC ACID.

The statement that tribromphenolbromide reacts with potassium iodide according to the equation

$$C_6H_2Br_3OBr + 2KI = C_6H_2Br_3OK + KBr + I_2$$

is founded on experiments of Weinreb and Bondi.[1] and of Werner.[2] The former obtained 95 per cent. of the theoretical iodine by digesting for twelve hours with an aqueous solution of potassium iodide at 18°, or 99 per cent. at 50°; the latter, using a chloroform solution, obtained 99.96 per cent. The more recent experiments of Kastle,[3] however, show that in chloroform solution, in absence of water, hexabromphenoquinone is the sole product, in which case only half of the iodine called for by the above equation is liberated; while if a carbon bisulphide solution of tribromphenolbromide be treated with an aqueous solution of potassium iodide, the iodine liberated varies from 90 to 100 per cent. of the theoretical amount, depending upon the relative quantities of potassium iodide, water, and carbon bisulphide present. In none of my own experiments, the results of which are detailed in Tables VII and VIII, did I obtain a quantitative yield of iodine; although potassium iodide was present in excess, the acidity of the solution was varied, different solvents were tried, and the digestion was much more prolonged than would be convenient in an analytical method.

It is apparent, however, that as the amount of tribromphenolbromide is reduced, the amount of iodine liberated approaches nearer and nearer to the theoretical value.

TABLE VII.

Expt.	Tribromphenolbromide. Gram.	Solvent.	Time.	n HCl. cc.	Iodine. Per cent.	Chloroform or benzene residues.
i	0.2038	none	7 days	..	77	
ii	0.2031	"	7 days	..	78	
iii	0.1747	$CHCl_3$	24 hrs.	..	87	Brown, not green with benzidine.
iv	0.1560	$CHCl_3$	20 hrs.	2.5	91	Deep red with aniline
v	0.1775	$CHCl_3$	8 hrs.	2.5	88	Yellowish red; not green with benzidine.
vi	0.2520	C_6H_6	48 hrs.	..	76	Deep red with aniline.
vii	0.2685	C_6H_6	36 hrs.	5	81	" " " "
viii	0.3045	C_6H_6	24 hrs.	5	84	" " " "
ix	0.2073	C_6H_6	10 min.	5	78	Green with benzidine.

[1] *Monatshefte f. Chem.*, **6**, 506 (1885).
[2] *Bull. Soc. Chim.*, **43**, 373 (1885).
[3] *Am. Chem J.*, **27**, 31 (1902).

Expt.	Tribromphenolbromide. Gram.	Solvent.	Time.	n HCl. cc.	Iodine. Per cent.	Chloroform or benzene residues.
x	0.2594	C_6H_6	1 hr.	5	80	Green with benzidine.
xi	0.0017	$CHCl_3$	5 min.	5	98	Too dilute.
xii	0.0034	$CHCl_3$	5 min.	5	94	" "
xiii	0.0068	$CHCl_3$	5 min.	5	91	" "
xiv	0.0102	$CHCl_3$	5 min.	5	87	" "
xv	0.0170	$CHCl_3$	5 min.	5	83	" "

In Experiments *i* to *x* the amount taken for analysis was weighed out and placed in a 100 cc. glass-stoppered bottle, the benzene or chloroform (10 cc.) added, then the acid and finally the potassium iodide dissolved in water. In Experiment *v* four times the theoretical amount of potassium iodide was used, in the others twice. The mixture was well shaken and allowed to stand for a measured time, at the end of which the iodine set free was titrated against N/50 thiosulphate. The results of the analyses are entered in the table under "Iodine" as percentages of the amounts of iodine that would have been liberated from the tribromphenolbromide taken had the reaction proceeded according to Werner's equation.

In Experiments *xi* to *xv* a weighed quantity of tribromphenolbromide was dissolved in chloroform, and a measured volume of this solution made up to 10 cc. for each experiment, 5 cc. of normal potassium iodide and 5 cc. of normal acid were added, and the mixture was well shaken and allowed to stand for five minutes, after which the iodine was determined as before.

After completing the analysis, the color of the chloroform or benzene solution was noted, and then a few drops of the aniline or benzidine reagent added. In Experiments *iv*, and *vi* to *x*, the presence of unaltered tribromphenolbromide was established, but in Experiments *iii* and *v*, although the chloroform solutions were colored, no tribromphenolbromide could be detected. This shows that in the experiments in question the deficit of 15 per cent. or so in the iodine is due to the formation of a by-product, and not to the incompleteness of the reaction formulated above. The delicacy of the benzidine test is not sufficient to enable it to be of value in Experiments *xi* to *xv*.

The experiments of Table VIII were carried out in the same way as the first ten of the preceding table, except that the hydrochloric acid was replaced by acetic, and an excess of sodium thiosulphate (5 cc. of a normal solution) was added to the reacting

mixture at the same time as the potassium iodide. The results are very similar to those of Table VII, and show that the deficit is not altogether due to the presence of iodine.

TABLE VIII.

No.	Tribrom-phenol-bromide. Gram.	Solvent.	Time. Hours.	n HAc. cc.	Iodine. Per cent.	Chloroform or benzene residues.
1	0.3195	C_6H_6	24	..	87	No reaction with benzidine.
2	0.1470	C_6H_6	20	5	95.8	" " " "
3	0.1795	C_6H_6	18	5	95.6	" " " "
4	0.2145	C_6H_6	24	5	92.1	" " " "
5	0.2748	$CHCl_3$	24	5	93.3	" " " "

From these experiments it is apparent that if in a phenol determination part of the tribromphenol precipitate is converted into tribromphenolbromide, the latter will not be quantitatively transformed into tribromphenol by the action of potassium iodide, and an error will thus be introduced into the analysis.

SUMMARY.

(1) Aniline and benzidine may be used as qualitative reagents for tribromphenolbromide.

(2) Tribromphenolbromide is quantitatively reduced to tribromphenol by zinc and sulphuric acid; a convenient method for its determination, based on this reaction, is described.

(3) Tribromphenolbromide is not a primary product of the action of bromine on phenol, but is formed by the gradual action of bromine water on tribromphenol. As the rate of this reaction is decreased by adding acid or potassium bromide, and increased by adding water or bromine (or by raising the temperature), it is probably due to the presence of hypobromous acid in the bromine water.

(4) Tribromphenolbromide is not quantitatively reduced to tribromphenol by hydriodic acid under conditions convenient for analysis; this is due in part to the formation of other products.

My thanks are due to Prof. W. Lash Miller, at whose suggestion this research was undertaken and under whose supervision it has been carried out.

THE UNIVERSITY OF TORONTO,
June, 1904.

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No. 53: THE CHEMICAL INDUSTRIES OF THE DOMINION

BY W. R. LANG

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THE CHEMICAL INDUSTRIES OF THE DOMINION.

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PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF TORONTO.

(*Read 10th December*, 1904).

(*Completed for publication, April*, 1905).

PREFACE.

MUCH of this paper appeared about two years ago in the *Journal of the Society of Chemical Industry*.* Recently it was communicated by request to the Canadian Institute after having been revised and, in a measure, brought up to date. A closer scrutiny of the subject matter, however, led to the conclusion that entire revisal and rewriting were necessary in order that it might present the condition of the chemical industries of the Dominion as they are at the time of publication. Every effort has been made to do this as far as possible, and the writer hopes that any shortcomings will be brought to his notice.

In writing on such a subject as the Chemical Industries of Canada, two main considerations have been kept in mind; firstly, that the development of the industrial resources of the Dominion during the past decade has been phenomenal, and secondly, that the extent of these developments is only fully understood by a few. While it is impossible to discuss *all* the industries in which chemical operations and reactions are made use of, an attempt has been made to select processes in some cases peculiar to the country, but notably the industries which owe their development to the natural mineral and vegetable resources, and to the widely scattered water power obtainable in the Dominion.

The subjects taken up may be classified as follows:—

I.—Common Salt and Alkali.
II.—The Extraction and Refining of Metals.
III.—The Manufacture of Leather.
IV—Sulphuric Acid, Acetic Acid, Wood Alcohol, Charcoal, and Ammonia
V.—Soap and Glycerine.
VI.—Refined Chemicals and Drugs.
VII.—Fertilizers.

* Journal of the Society of Chemical Industry, May 15th 1903

VIII.—Coal-Tar and Asphalt.
IX.—Calcium Carbide, Carborundum, Corundum and Graphite.
X.—The Cement and Plaster Industry.
XI.—The Beet-Sugar Industry.
XII.—Natural Gas and Petroleum.
XIII.—Pulp and Paper.
XIV.—Asbestos and Mica

I.—COMMON SALT, ALKALI AND CHLORINE COMPOUNDS.

Sodium chloride is found in the upper silurian beds in Ontario, and in the Devonian in Manitoba and Athabasca; salt springs also occur in Cape Breton and in New Brunswick, but these are comparatively unimportant sources of supply. In Ontario the salt area stretches through the counties of Middlesex, Huron, Bruce, and Lambton, large deposits being found along the shore of Lake Huron from Kincardine to Windsor. At Goderich there is a deposit 126 feet thick, and at Windsor a well extending to a depth of 1,672 feet passes through four beds of rock salt of an aggregate thickness of 392 feet.[1] The salt is obtained by evaporation, and is of an excellent quality. The following comparison serves to illustrate the purity of the natural product.[2]

	Natural Salt of Goderich, Ontario.	Natural Salt of Cheshire, (England.)
	Per Cent.	Per Cent.
Sodium chloride	99.687	96.70
Calcium chloride	0.032	0.68
Magnesium Chloride	0.095	0.00
Calcium sulphate	0.090	0.25
Moisture	0.079	0.63
Insoluble matter	0.017	1.74
	100.000	100.000
Total Impurities	0.234	2.67

The total production of salt in Canada was valued in 1892 at $162,000, in 1901 at $262,328, and in 1903 at $334,000.[3 bis.]

Apart from its use as a seasoning and as a preservative, common salt is employed in the electrolytic preparation of caustic soda and bleaching compounds.

The alkali and bleaching powder industries throughout the world

(1) W. Hodgson Ellis, M.B., in "A Handbook of Canada," 1897.
(2) Wilmott, A.B., "Some Minor Minerals of Canada," 1897.
(3 *bis.*) Statistical Year Book, 1903.

are at the present time in an unsettled condition, mainly owing to the advent of electrolytic methods.[3] Wherever cheap water power is available, however, electrolytic processes will be rapidly developed, provided the raw material is obtainable within a reasonable distance.

II.—THE EXTRACTION AND REFINING OF METALS.

Almost every province in the Dominion possesses valuable mineral resources; these are rapidly being exploited, and among the metals produced in quantity may be mentioned iron, copper, lead and silver, nickel, arsenic, antimony, and, lastly, aluminum. These metals are found in the form of native iron, magnetic iron ore, iron pyrites, hæmatite, native copper, chalcopyrite, galena, native silver and ores of silver, nickeliferous pyrrhotite, gold, sulphide of antimony, and arsenical pyrites.

IRON.

The iron ores of the Dominion occur at varied intervals, from Vancouver Island on the west to Cape Breton Island and Newfoundland on the east. In Nova Scotia there are particularly rich deposits, and in close contiguity to them are found the necessary materials for smelting. Hæmatites, too, are found in all parts of Canada. One of the most valuable deposits of specular iron is at Hull, near Ottawa, which assays from 64 to 68 per cent, of metallic iron. In the Appendix (Appendix I.) will be found more particulars regarding the iron ores of the Dominion.

The Canadian iron industry dates back to the establishment of the St. Maurice forges by the French Government in 1737. Many other minor plants were subsequently built, as at Batiscan, Hull, and Bois de Paul, all in Quebec; at Furnace Falls, Mormondale, Marmora, etc., in Ontario; at Woodstock, in New Brunswick; and at Moose River, Nictaux, and Bloomfield, in Nova Scotia. They all subsequently failed, however, in consequence of the competition of Great Britain and the United States. This early failure was due as much as anything else to lack of enterprise, capital, and proper shipping facilities. The modern development of the industry may be said to date from the introduction of a protective duty on iron in 1887. The granting of bounties by the Dominion and Ontario Governments has also assisted largely in bringing about the present condition of the iron and steel industries.[4] The annual aggregate capacity of the completed and unfinished furnaces in the Dominion in 1903 was

(3) Chem. Tr. J., 23.8.02, 6.9.02, and 24.1.03.

(4) Dominion bounty on pig iron, $3 per ton produced. Ontario bounty $1 per ton on pig iron produced from Ontario ores, and 50 cents on ores not obtained in the Province; the rate of $1 to be only paid up to 25,000 tons. Bounty is at present largely reduced owing to increased production.

close on 1,000,000 gross tons.[5] Much of the iron produced is now being made into steel[6] by the Bessemer process. At Sault Ste. Marie there is an extensive plant with a capacity of 200,000 tons of ingots and 180,000 tons of finished products. There, steel rails are being made to the extent of 500 tons a day. This company has its own blast furnaces, and undertakes all the processes, metallurgical and mechanical, through which the metal goes in its conversion from ore to finished product.

At Collingwood, Ontario, the Northern Iron and Steel Company, which recently acquired the works of the Cramp Steel Company, have two 20-ton open hearth furnaces besides rolling mills from which will be turned out material suitable for machinists' and blacksmiths' use, finished steel bars, angles, fish plates, tie plates and small sections such as are used by many manufacturers. The Gilchrist Thomas is the process employed, a process which allows of ores containing phosphorus, for example, to be profitably converted into good uniform steel. The ten inch mill at the Collingwood works is equipped with underground tunnels and turtle-backs for the purpose of continuous rolling, that is to say, a bar of steel will be looped from one pass of the rolls into another pass: thus a mill of this description is enabled to roll rods and long bars. The furnaces are of the latest standard design, having air cooled end blocks and slag pockets with the regenerators under the charging platform, which is of steel and concrete.[7] Recently the sompany has begun to convert, by "cold-drawing," steel bars into wire of various gauges.

The Canada Iron Furnace Company has its principal plant at Midland, Ontario, besides several other smaller establishments in various parts of Quebec. The Midland furnace was erected during 1899-1900 on a property about 100 acres in extent, situated on the north shore of the Midland Bay. The furnace proper has a capacity of from 120 to 140 tons a day of "Midland Brand" Foundry Malleable Bessemer and Bessemer Pig Iron, and is marketed almost entirely in Ontario. The raw materials used are coke, iron ores and limestone. The coke is obtained from the Connellsville district in Pennsylvania, and is brought in by rail. The iron ores are brought in by vessel from Canadian and United States ports on Lake Superior and also Lake Michigan. The limestone is obtained from the company's own quarry, which is about 130 acres in extent, situated about three milles from the furnace. This material is brought to the furnace by scows in the summer and by teams in the winter.[8]

(5) In a letter from Mr. T. W. Gibson, Director of the Ontario Bureau of Mines, the following figures are given for 1903:

Pig Iron produced in	Ontario	.....	87,004	tons.
Steel	"	"	15,229	"
Pig Iron	"	Canada	265,418	"
Steel	"	"	232,641	"

(6) Dominion bounty on steel, $3 per ton; $2 per ton on steel from foreign ores.
(7) Letter from Mr. J. A. Currie.
(8) Letter from Mr. A. C. Adams, Midland.

On the eastern seaboard of the Dominion are situated the works of the Dominion Iron and Steel Company, begun in 1899. Coal and limestone are found comparatively near at hand, the farthest afield mine from which the coal supply is drawn being twenty-five miles distant, while the nearest one is six miles. Nearly all the iron ore at present used is brought from mines owned by the company on Great Belle Island in Conception Bay, Newfoundland, some 400 miles from Sydney. This mine is estimated to contain 28 million tons of available ore, besides areas under the sea, which are believed to be very extensive. Analyses of the ore show it to contain fifty per cent. of iron, little sulphur, but rather too much silica, aluminium, and phosphorus. The result is a pig iron too high in phosphorus, but during the subsequent conversion of the pig into steel in open-hearth furnaces, this impurity is eliminated, and a fine quality of steel produced. For the best kind of pig iron, it is necessary to mix other ores with it, and for this purpose Cuban, Spanish, and Swedish ores are used, the result being a low phosphorus pig. Indications of large deposits of high-grade ores have been found both in Nova Scotia and Cape Breton, which, when fully developed, will in a great measure replace the foreign ores.

Limestone is obtained from the company's quarries at the Bras d'Or Lakes, about eighty-five miles, by water, from the works. It is a stone of good quality, and is found in large deposits; it acts well with the Newfoundland ore and the Cape Breton coke[8 *bis*]. The works contain four blast-furnaces capable of yielding 1,000 tons of pig iron per day; the furnace gases are utilized also to the utmost, being used to heat the blast and also to raise steam. The iron produced is partly cast into pigs and in part conveyed in a molten condition direct to the open-hearth furnaces, where it is converted into steel. Of these there are ten in number of the H. H. Campbell type of tilting basic open-hearth furnaces, having a capacity of fifty tons each. A very complete arrangement of testing the steel at intervals is in vogue, and of stamping each ingot with special marks so that the consumer can ascertain from the company at any time every particular regarding the analysis and making of the piece.

The gases produced in the coke ovens are used in the opening hearth furnaces, the other bye-products, namely, coal-tar and ammonia, being also collected. The ammonia is converted into sulphate of ammonium by neutralizing it with sulphuric acid—which can be obtained from the pyrites separated from the coal in the preliminary grinding and washing processes to which it is subjected, and is principally exported to the United States, the West Indies, and Glasgow.

(8 *bis*.) The daily shipment is 1,500 tons.

Canadian-made steel is largely exported to the United States from where it returns to this country in the form of rails and other finished products; but it is intended that this feature of the steel industry will shortly be transferred to Canadian territory. Sydney is extremely well situated as a seaport, being nearer to England than is New York, and, strange as it may appear, to the ports of South America and South Africa.[9] As far as the geographical position is concerned, therefore, Sydney possesses many advantages, while the masterly and liberal way in which the iron and steel industry has been organized and developed, points to a bright future for it in Canada.[10]

A new plant has been erected near North Sydney by the Nova Scotia Steel Company, who have at present works at Ferrona, with a limited supply of ore near at hand. Hence they import largely from Newfoundland. Their steel works are at present at New Glasgow, but a new plant is under construction at Sydney (1903), Their output, which is sold almost exclusively in Canada, approximates 100 tons of pig-iron per day and the same amount of steel.[10 *bis*.]

COPPER.

The production of refined copper can hardly be classed among the chemical industries of the Dominion, as practically only the first stage in its extraction of the metal is reached, namely, the making of copper matte, which is exported to the United States to be refined. As will be seen below, however, the refining of this metal is now being carried on in British Columbia.

Copper ores occur in great abundance, and constitute one of the most important mineral resources of the country. These are distributed over large tracts in Ontario, Quebec, Nova Scotia, and New Brunswick. The deposits consist of native copper and sulphides, the former confined principally to the Lake Superior region, the latter being more widely diffused,

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	Miles.
(9) Sydney Harbour to Liverpool (*via* South of Ireland)	2,307
New York Harbour to Liverpool	3,110
Sydney Harbour to Pernambuco	3,567
New York Harbour to Pernambuco	3,696
Sydney Harbour to Cape Town	6,467
New York Harbour to Cape Town	6,787

These figures were supplied to me by Mr. Watson Griffin, who obtained them from Captain W. H. Smith, R.N.R., Halifax. The distances from New York were compiled by the United States Commission of Navigation.

(10) Mr. Watson Griffin, who kindly supplied me with material from which the above description of the Sydney operations was written, mentioned also that a leading Scottish iron and steel magnate told him that, everything considered, Sydney, in regard to raw materials, nearness to the mark and the excellent equipment it possessed, would be the finest steel manufactory in the world. Watson Griffin, "Dominion Steel and Coal Co., Sydney;" Montreal, 1902. Watson Griffin, "The Front Door of Canada;" Montreal, 1899.

(10 *bis*.) The production of pig iron in 1903 amounted to 265,418 tons, as compared to 47,000 tons in 1893, while the proportion of the home product to the total consumption of pig was 76 per cent. in 1903 as compared with 42 per cent. in 1893.

but notably in the Sudbury region, Ontario, where it occurs with nickel. The production of copper, other than the native copper near Lake Superior, is dependent for the most part on that of this latter metal.

The British Columbia Copper Company is now turning out about seven million (7,000,000) pounds of copper a year and has an excellent converter plant at its mine. This copper is produced at a cost of about 9½ cents a pound. The product from the converter is blister copper and is sent to New York to the Nicholls Chemical Company to be refined. The Montreal and Boston Copper Company is now producing about 3,000,000 pounds of copper and is selling its matte to the British Columbia Company. The Granby Company is producing about 15,000,000 pounds of copper a year, at a cost of around 9½ cents, laid down in new York.[11]

Some idea of the advances made in the production of copper matte may be had from the fact that in 1893 the production amounted to 8,000,000 pounds, while 1903 showed an output of 43,000,000 pounds.[11 *bis.*]

Mr. A. P. Turner of the Canadian Copper Company at Copper Cliff, Ontario, has furnished some interesting particulars regarding the production of copper as carried on at the works of this company, which controls about 20,000 acres of mineral lands in the nickel district extending from Garson Township in the District of Nipissing, south-west to Drury Township in the District of Algoma, in the Province of Ontario. The company began operations in 1887, and at present is mining and smelting about 700 tons of ore per day. The ore is a mixture of nickeliferous pyrrhotite, pentlandite, chalcopyrite and diorite. The nickel in this pyrrhotite replaces about two to four per cent. of the iron. Copper occurs in the form of copper pyrites. The ore contains no arsenic or antimony, but small traces of gold, platinum and palladium. An average assay of the different mines is about two per cent. copper and four per cent. nickel.

The company has designed and just finished at Copper Cliff, a new smelting and power plant, in which are combined the latest and best improvements in the smelting world. There are larger plants, but it is doubtful if there is another in which are assembled so many up-to-date conveniences for every part of the work.

NICKEL.

The first discovery of nickeliferous deposits was made in 1883 near Sudbury, in the district of Algoma, Ontario. Previous to the discovery of nickel in this country, the French colony at New Caledonia practically

(11) Letter from Mr. F. P. Clappison.
(11 *bis.*) Statistical Year Book, 1903.

contributed the world's supply of the metal, though supplemented, in a small degree, by the Gap Mine in Pennsylvania, and by a few isolated mines in Norway and Hungary. Professor Coleman[12] states that the Sudbury ores consist of a mixture of pyrrhotite (magnetic pyrites) and copper pyrites, and in this resemble the gold ores of Rossland. In order to obtain the metal the ore is smelted into a matte, containing from twelve to twenty per cent. of nickel and about the same amount of copper, is "Bessemerized" into a regulus containing about forty per cent. of nickel and is shipped to Clydach in Wales, where its nickel content is extracted and refined by the process invented by Dr. Ludwig Mond, F.R.S., and which bears his name. The chemical principle on which this process is based is the formation, at temperatures of about 50° C., of a volatile colourless gaseous compound of nickel and carbon monoxide of composition Ni_4CO, which, on being subjected to a temperature of 180° C., decomposes, leaving metallic nickel and liberating the carbon monoxide. The product thus obtained contains between 99.4 and 99.8 per cent. of nickel. The Mond Nickel Company is the only company refining nickel within the British Empire, and it is interesting to note that at the recent St. Louis Exhibition Dr. Mond was awarded the gold medal for his process, the company receiving a similar honour struck in silver.[13] Nickel from Canadian ores is now being used in the manufacture of armour plate in constructing ships for His Majesty's navy.

What is known as the Orford or alkaline sulphide process of refining nickel is the one by which the Canadian Copper Company's mattes are treated at Constable Hook, N.J., by the Orford Copper Company. As this company (now forming part of the International Nickel Company) is the chief producer, the bulk of the nickel ores of Ontario are refined by the Orford process. An electrolytic refinery erected by the Canadian Copper Company at Cleveland, Ohio, was operated for a short time only, but shut down in 1902.[14]

The Orford Copper Company is also producing *palladium*. This metal belongs to the platinum group, and is found associated with it. The Sudbury ores are said to contain from one tenth of an ounce to one ounce per ton, and Dr. Joseph Wharton, in an article recently published [14 *bis*.] prophesies a future production of palladium from these deposits. Palladium is an interesting metal, not only from the chemist's point of view, but also from an industrial one, as its physical properties, hardness, etc., and the difficulty with which it is attacked and tarnished at atmos-

(12) 8th Report of Bureau of Mines, Ontario, page 106.

(13) A full account of the Mond Nickel Process will be found in the 8th Report, Bureau of Mines, Ontario.

(14) Letter from Mr. T. W. Gibson, Director of the Bureau of Mines, Ont.

(14 *bis*.) "Hardware and Metal," Dec. 3rd, 1904.

pheric temperatures, render it eminently suitable for replacing silver as a reflecting surface on optical instruments, for plating the finely cut scales on instruments of precision and for alloys.

ALUMINUM.

The extraction and refining of aluminum has in recent years, owing to the advent of electricity developed from cheap water power, become an important industry. At Shawinigan Falls, Quebec, are situated the Canadian works of the Northern Aluminium Company, a sub-company of the Pittsburgh Reduction Company, which also has two large factories at Niagara Falls, N.Y. The raw material, bauxite, is obtained from Alabama, Arkansas and Georgia, in the United States. The process employed is the Hall[15] process, and is a combined electrolytic and electric furnace one. The native aluminum hydroxide is first purified by mixing with sufficient carbon to reduce all impurities in it to the metallic state, the resulting iron, mixed with titanium and silicon, forming a slag after melting the mass in an electric furnace. An alternating current of low voltage is used, and the purified alumina separates out above the slag in an almost chemically pure condition. The alumina thus purified is then electrolyzed in a bath containing cryolite at a temperature of from 850° to 900° C. The action of the current sets free aluminum and oxygen, the latter uniting with the carbon anodes to form carbonic oxide. The metal is run into rough ingots weighing twenty pounds each, and is stated to contain, on an average, 99.5 per cent. of aluminum.[16] The principal portion of the product at Shawinigan is shipped in the form of ingots, although there is in addition a wire mill where aluminum wire and cable for electrical conductors are made.

The production of the Quebec works is probably 9,500 pounds per day, the value in 1902 being approximately $1,043,250.[17] It may safely be said that the three works of this company between them produce one-half of the world's supply.

LEAD AND SILVER.

These metals are derived principally from the mines of British Columbia, but there are also deposits of galena along the shores of Lake Superior, the ore from which is sent to Niagara Falls, N.Y., for reduction. The British Columbia ore is a high grade one, carrying from 25 to 300 ounces of silver to the ton. At Trail, in British Columbia, the Canadian Smelt-

(15) Dr. J. W. Richards in "Electro-Chemical Industry," Oct., 1902.
(16) *Ibid.* (average value of product is 31 cents per pound).
(17) Canadian Mining Rev., March, 1903.

ing Works have recently begun to produce commercial lead, stated to be of 99.9 per cent. purity,[18] by means of the Bett's process, which is an electrolytic one.

The Hall Mining and Smelting Works, whose Canadian headquarters are at Nelson, British Columbia, are smelting lead ores which are obtained in the Slocan and Kootenay Lakes. They employ blast furnaces, a considerable portion of the ore being first roasted in hand or mechanical furnaces, and the product of the latter briquetted. The principal markets for the pig lead are the Orient, England, and Canada, though the home market is somewhat handicapped by the present arrangement of duties, which allows the importation of foreign corroded lead at a lower rate than that imposed on pig-lead. With a revisal of the duties a greatly increased development and revival of the lead and smelting industries is anticipated.[19] *bis.*

In 1894 the amount of silver exported, in ores, concentrates, or otherwise, was 629,655 ounces, while in 1901 the quantity had risen to over 4,000,000 ounces.[19] Despite these figures, the *Monetary Times*, Toronto, of date January 16th, 1903, says, "The silver-lead production of British Columbia is severely handicapped by the adverse competition of the United States, the European and Mexican products. The tariff is unfavourable; a higher one would be quite beneficial to the industry."

During the session of 1903 the Parliament of Canada provided for the payment of a bounty of 75c. per hundred pounds on lead smelted in Canada from Canadian ores, the maximum amount of bounty payable in any one year being $500,000, and the rate subject to proportionate reduction when the standard price of pig lead in London, England, exceeds £12 10s. per ton of 2,240 pounds. This provision has led to the revival of silver-lead mining in British Columbia. A small plant for smelting lead has been erected at Bannockburn, Ont., to be used on the non-argentiferous ores of that locality.[19 *bis.*]

ARSENIC.

A not unimportent metal found in considerable quantities in Ontario is arsenic; the chief form in which it occurs is arsenical pyrites (mispickel), which also contains gold. Its manufacture was begun by the Canadian Goldfields, Limited, at their Delora Mine, Hastings County, Ontario, in 1899. Attempts had been made, extending over the previous twenty years or so, to extract the gold from the ore found there, and, after the mine had experienced some vicissitudes, the present company acquired

(18) Letter from the Business Manager, Hall Mining and Smelting Co., Nelson, B.C.
(19) Statistical Year Book of Canada, 1901.
(19 *bis.*) Letter from Mr. T. W. Gibson.

it and obtained the rights (1896) for Ontario to the Sulman-Tweed patents (bromo-cyanide process), working it with only a modified degree of success for a couple of years, when the installation of improved machinery and the adoption of a combination of amalgamation and leaching with bromo-cyanide resulted in the recovery of arsenic from the mispickel concentrates. To accomplish this the concentrates are heated to a high temperature in specially constructed cylindrical revolving calciners, and the resulting impure arsenious oxide evolved is condensed in hermetically sealed brick chambers.[20] The crude arsenic is refined by sublimation, and contains from 99.6 to 100 per cent. arsenious oxide, the main impurity being silica in a finely divided condition.[21] It is exported chiefly to the United States, where it is used for making "Paris Green," etc. The output has increased from 113,477 pounds in 1899 to 1,347,000 pounds in 1901.[21] In time and with proper development Ontario should be able to supply the entire demand for arsenic on the continent of America.

Auriferous mispickel mines are being opened up at Lake Temagami, and concentrating works are in course of erection. The process of refining the arsenic will be an electrical one. The ores of the Haileybury region, not far distant, discovered last year, contain 60 or 65 per cent. of arsenic, but are more valuable for their other constituents, including silver, cobalt and nickel.[19] *bis*.

ANTIMONY.

This metal might almost be said to occupy the position of a bye-product in the extraction of gold. At Rawdon, in Nova Scotia, the ore (stibnite) is auriferous, and from 1898 to 1901 no refined antimony was produced, the stibnite being mined for the sake of its more precious contents[22]. It is also found in Quebec, and recent reports indicate deposits of ore in several localities of Ontario and British Columbia. The output in 1891 had fallen to $60. In 1902 the refining of the metal was renewed.

GOLD.

Gold is mined to a small extent in Ontario, in Nova Scotia and Quebec. Gold deposits are also found in the Kootenay district, B.C., in Cariboo, B.C., and in the Yukon. In the Rossland district the ore is a cupriferous pyrrhotite under a diorite cap, and from Trail on the Columbia River, where the

(20) C. Kirkegaard, in Eng. and Mining J., Jan. 31, 1903.

(21) Bureau of Mines Report, Ontario, 1901.

(22) Assays of two ores give, according to the Nova Scotia Mines Report, 1901:—

	I. Per cent.	II. Per cent.
Antimony	45.75	18.21
Gold (oz. per ton)	2.48	0.23
Silver (oz. per ton)	0.10	0.13

ore is smelted, the gold-copper matte produced is shipped to Montana for refining purposes. There is also a smelter at Nelson for the ore of the Hall mine. The Yukon territory covers in a general way the district north of Cariboo, south of the Arctic Ocean, and lying between the Mackenzie River and the Alaska-Canada boundary. Gold has been known to exist there since 1864, and has been worked intermittently since 1873. Forty Mile River, a tributary of the Yukon, was discovered to carry coarse gold in 1886, and ten years later, what is known as the Klondike, was found to contain gold also, It was first discovered on Bonanza and Eldorado creeks;[23] the news of this discovery spread far and wide, and active prospecting was the result. There are about 1,400 miles of Canadian Yukon streams, on all of which gold can be found. Mr. Ogilvie, former Canadian commissioner in the Yukon, estimates that an area of 125,000 square miles is gold bearing.[24] The former difficulties of reaching the Yukon have now been overcome; a telegraph line has also been laid by the Canadian Government from Skagway, on the coast, to Dawson. The gold is found and worked in the gravel deposits of the valleys and on their adjacent slopes, and it has been estimated that gold to the value of 95,000,000 dols. will be produced from these deposits in the next few years.[25]

The gold fields of Nova Scotia occupy the entire Atlantic coast line, and contain gold in combination with sulphides and arsenides of iron, but mostly in the free state. The following table will best convey the output of gold from Canada and its distribution.[26]

	1892	1901
	Dols.	Dols.
Ontario	7,118	243,022
Saskatchewan, N.W.T.	98,006	15,000
Yukon	.....	12,500,000[27]
Quebec	12,887	3,000
British Columbia	399,525	5,596,700
Nova Scotia	389,965	604,500
Total	907,601	18,962,222

The gold production for the Yukon in 1902 was 12,018,561 dols.; according to the United States Mints it was 14,525,275.[28]

The total output of gold in Canada in the years 1893, 1900 and 1903 amounted respectively to $976,603, $27,908,153, and $18,834,373. The figures for 1904 are not yet available.

(23) "Official Guide to the Klondike," by William Ogilvie.
(24) *Ibid.*
(25) Report of the Canadian Commission in the Yukon.
(26) Statistical Year Books, 1892-1902.
(27) Letters from Mr. B. E. Walker, General Manager, the Canadian Bank of Commerce.
(28) Letter from Hon. Clifford Sifton, Minister of Interior, Ottawa.

III.—THE MANUFACTURE OF LEATHER.

The manufacture of leather has, during the last thirty years, occupied quite a prominent position in Ontario and Quebec, and, during the past few years, through the stimulus from a larger home market and increasing sales to foreign markets, has grown greatly. As compared with a decade ago the value of the leather produced in the country may safely be said to have doubled. There are from eighteen to twenty large establishments in operation and fully fifty small ones. No tanning is done in the North-West Territories, and practically none in British Columbia. Bark, chrome, and combination tanning methods are employed, the spent bark being utilized in large establishments in specially constructed furnaces. Though the United States may be said to lead the world in the extent of leather produced, the quality of the Canadian product is not surpassed. The Canadian specialties are hemlock sole and harness, black and coloured shoe leathers, coloured and fancy side leathers for the bag, trunk and saddle trades. In Toronto there are several sheep-skin tanneries as well.

Speaking generally Quebec supplies the cheapest grades of leathers, chiefly black; Ontario the better finished lines both black and coloured. A portion of the American patterned machinery employed and formerly imported is now being manufactured in the Dominion, such as bark mills, fleshing machines, glazing jacks, drums and presses; but the most expensive and elaborate machinery is still made in the United States. The import duty on machinery is 25 per cent. The manufacture of hemlock extract in New Brunswick has already had a beginning, and will doubtless grow as the prices of bark and labour advance.

IV.—SULPHURIC ACID, ACETIC ACID, WOOD ALCOHOL, CHARCOAL AND AMMONIA.

The manufacture of commercial sulphuric acid has not yet been developed to the extent that the quantity of sulphur found throughout the Dominion would justify. There is enough sulphur in Canada to supply the entire home market with acid and even to develop a considerable export trade. Only a few firms, however, are engaged in the trade, and a large portion of their product is used in the refining of Canadian petroleum, some five million pounds being annually consumed for this purpose. Quebec, Ontario, and British Columbia are each represented in the acid industry. It is probable that the construction of electrolytic lead smelters will lead to the sulphur dioxide obtained from the galena being made into sulphuric acid, as is done at the Electric Lead Reduction Company's works at Niagara Falls, N.Y., where, it is stated, the sulphuric acid produced

yields a financial return sufficient to cover the entire cost of the process.

At London, Ontario, the Canada Chemical Manufacturing Company turns out about fifteen tons of sulphuric acid per day; brimstone, imported from the States, is used, and is preferred to the Sicilian sulphur. This company does not use pyrites on account of the arsenic it contains. The process employed is the chamber one, indeed, as far as the writer knows, the "contact" process has not yet been tried in Canada. Sulphuric acid is used by many manufacturers, such as tack, screw, nail, leather and fertilizer makers, wholesale druggists, dyers and oil-refiners.' Phosphates of calcium and sodium are also made by this company, native phosphates and the animal charcoal (bone black) rejected by sugar refiners serving as sources of phosphorus. The acid phosphate of calcium is employed in the baking-powder trade instead of cream of tartar, and is claimed to be less costly, to keep better, and to restore to the flour the phosphates which, by the modern methods of milling, have been removed from the wheat.

Sulphites, bisulphites, crude acetic acid from the grey acetate of lime, chlorides of zinc and iron and Glauber's salts are likewise made.

By the destructiye distillation of wood, acetic acid, wood alcohol and charcoal are obtained; hence Canada, with its enormous supply of wood of all kinds, should be able to take a prominent place in the production of acetic acid and wood spirit. At the present time the residual charcoal from the retorts does not find a ready market, owing to the comparatively high rates for transport as compared with other fuels, weight for weight. The outlook in this direction is, however, brightening. Among the firms engaged in this manufacture might be mentioned the Standard Chemical Company, with plants at Fenelon Falls, Deseronto and Longford, Ontario, and Cookshire, Quebec; the Canada Paint Company, Montreal and Toronto; and the Lake Superior Power Company, which is said to have the largest retort plant in the world. Very keen competition has to be faced in this connection with the United States, as a combination of some 175 manufacturers practically controls the market. The crude acetate of lime produced in the distillation process is converted into acetic acid, some of which is sold for dye and colour-making purposes, while a considerable portion is exported to Europe and Australia.

The wood alcohol, obtained at the same time as the acetic acid, supplies the home market and is also exported largely to Great Britain, France, Germany, Holland, Japan, and Australia. It may be of interest to know that timber is imported from Canada by makers of wood alcohol in the United States.[29]

(29) Mr. Webster, of the Standard Chemical Co.

The total production of ammonia from all the gas liquors obtained in the destructive distillation of coal throughout the Dominion is, the writer is informed by Mr. J. G. Harvey of Toronto, about 235,000 pounds of a 28° Beaumé solution. As this quantity is in excess of what is required to supply the Canadian market by some 100,000 pounds, that amount is exported to the States. Besides the numerous trade preparations of ammonia used for household and other purposes, "aqua ammonia" and anhydrous liquid ammonia are the two principal forms in which it is prepared. The process consists in mixing milk-of-lime in suitably constructed vessels with the ammoniacal gas liquor, agitating and heating with steam and conducting the liberated ammonia through more milk-of-lime, through a drip-tank and, in succession, through oil, charcoal purifiers, caustic alkali and finally to tanks of distilled water kept cool by running water, where the gas is absorbed and the ammonia of commerce thus obtained. Manufacturers claim that the amount of water required to be used during the process reduces the profits considerably, as the gas-liquors are of a poor quality, seldom exceeding 1½° Twaddle. Anhydrous ammonia is produced from the "aqua ammonia" by a series of fractional distillations, is liquefied by pressure and stored in hundred pound welded iron cylinders. It contains 99 per cent. liquid NH^3, and finds its principal use as a refrigerant.

V.—SOAP AND GLYCERINE.

SOAP.

The soap industry in Canada is growing rapidly; at the present time some fifteen large concerns are in operation, employing in all about 2,000 hands. A branch of the well-known firm whose headquarters are at Port Sunlight near Liverpool, was recently started in Toronto, with an annual capacity of 10,000 tons. Their products are similar to those made at their other works, and their raw materials are procured from Africa, the United States, and locally (tallow). They own islands in the Pacific from which they import cocoanut oil.

Many other firms are also manufacturers on a large scale and produce all grades, from the cheapest textile and laundry soaps to the finer qualities of toilet soaps. Great advances have taken place in the industry during the past ten years, particularly in the making of the latter. The same system of manufacture obtains in England. The raw materials are mainly cocoanut oil, palm oil, and tallow, the first two in a large measure superseding the last mentioned. The market for Canadian made soap is limited, the home market is supplied and a large export trade is done with the West Indies and Australia. The competition of the United States is felt more

than that of England or France. In 1902 the value of the soap produced was approximately $3,000,000.[30]

GLYCERINE.

This necessary bye-product in the manufacture of soap is refined in some cases by the producers themselves; others sell it to firms engaged more particularly in the refining trade. Among these might be mentioned the St. Henri Chemical Company, of Montreal, who buy waste lyes from the soap manufacturers, recover the salt from the lye, refine the glycerine, and sell to the makers of nitro-glycerine. The capacity of these works is 10,000,000 pounds of waste lye yearly.[31]

VI.—REFINED CHEMICALS AND DRUGS.

There are very few makers of refined chemicals in the Dominion. The small demand for pure chemicals is mainly accountable for the lack of local manufacturers, the market being necessarily a small one, and most buyers of pure chemicals for laboratory uses are apt to demand articles of the make of one or other of the large and old established German or English houses. One can hardly doubt but that the Canadian maker must desire a higher tariff on imported material. Of heavier chemicals, however, the Canadian Process Co. has recently begun the manufacture and the work is proving very successful. Such products are bisulphite, sulphide, thiosulphate (hyposulphite), sulphite and sulphate of soda, lime, and zinc salts, lactic acid, casein, etc. Messrs. Lyman Bros. and Company are continuing to extend along the lines of refined chemicals, their gold and silver salts being much in demand. Along with these they produce and refine such high grade chemicals as chloroform, ether, iodide of potassium, bromides, scale preparations, iron and zinc salts, acids of phosphorus, syrups, tinctures, and flavouring extracts. Most of the raw materials are imported. In the drug department this firm has probably the best grinding machinery in Canada, where, besides their own work, they do a considerable amount of grinding for other firms. In the strictly pharmaceutical business, Messrs. Parke, Davis and Company, Walkerville; H. K. Wampole, Toronto; F. Stearns, Windsor; and John Wyeth and Bro., Montreal, have manufacturing establishments. Recently the brand "Made in Canada" has been much in evidence, and many buyers prefer such goods, even if they are slightly more expensive, to the imported article.

A few years ago the Liquid Carbonate Company of Toronto commenced the manufacture of carbon dioxide on a commercial scale, and is now

(30) Mr. Knight, of the Sunlight Soap Co.
(31) Letter from the President of the Company.

producing some two tons a day. The methods employed for obtaining the gas are from the action of an acid, such as sulphuric acid, on chalk, dolomite or sodium carbonate, and by the combustion of coke, while it is also got as a bye-product from the fermentation vats in breweries. The gas, after being washed and purified, is compressed, cooled, and in liquid form is forced into steel cylinders at a pressure of from sixty to eighty atmospheres. (The cylinders are tested to a pressure of over two hundred atmospheres). This liquid gas finds a market from the Atlantic to the Pacific, and is used for aerating mineral and artificial waters, for forcing beer from barrels in the cellar to a higher level, and at the same time preserving it from deterioration. It is also used in the refining of sugar, as a motive power in spraying trees with a germicidal solution, and in the laboratory for producing low temperature mixtures. Numerous useful bye-products are a consequence of the process of production of carbonic acid, such as fine clay used by paper-makers, Epsom salts and Glauber's salts—all of which are employed in many industries and command a ready sale.

VII.—FERTILIZERS.

Mineral phosphates, in the form of apatite, are found in the Ottawa Valley, Ontario, but the deposits have not been worked for several years. About 1891, in which year the phosphates mined were valued at $50,000, a falling off began in the output of this mineral, which continued up to 1902, when the amount mined was hardly worth recording. This industry is on the increase again, however, and last year saw a production valued at some $8,000. This state of affairs has been brought about mainly by the large supply of easily-worked phosphates found in Florida and Carolina, U.S.A., much of which is obtained by dredging. It may be mentioned, however, that a certain amount of apatite is made use of in the Province of Quebec by the Buckingham Electric Reduction Company, who manufacture phosphorus therefrom.[32]

Sulphate of ammonia is manufactured at the works of the Dominion Iron and Steel Company, Sydney, N.S., whose products are supplied to dealers and others engaged in the fertilizer business. The ammoniacal liquors of the Quebec, Ottawa and Toronto Gasworks are worked up at the latter city by the Michigan Ammonia Company.[33] In Montreal, one firm at least, makes sulphate of ammonia, and at one time the gas works there utilized their own liquors for its production. Latterly, however, the gas liquor was exported, to be dealt with by a firm in the United States.

Quite a number of other fertilizers are produced in the Dominion from

(32) Minerals of Quebec: published by the Provincial Government.
(33) Letter from Mr. Macfarlane, Chief Analyst to the Inland Revenue Department.

refuse matter, such as blood, tankage, bones, and offal, besides natural phosphates. Ontario, New Brunswick, Quebec, Nova Scotia, Prince Edward Island, and British Columbia, all produce fertilizers, more or less.[34]

VIII.—COAL-TAR AND ASPHALT.

Very little tar distillation is carried on in the Dominion, owing mainly to the tar produced in the gasworks being too thick for treatment with any degree of success. It is mainly used for saturating paper, which is employed largely as a waterproofing material by builders. Some is boiled down into pitch, but about one half of the tar produced is exported to the United States. There is a small distilling plant at Hamilton, Ontario, which the writer understands, was, up to eighteen months ago, the only one of its kind from which coal-tar oils were produced in Canada. The Dominion Iron and Steel Company at Sydney obtain a considerable quantity of coal tar from their coke-ovens. This, at one time, found a market in the States, in Montreal and other points in Canada, but recently arrangements were made w th an English chemical company to locate at Sydney with a view to utilizing all the coal-tar produced from the coke-ovens. The works, which are one of the largest on the continent, are now in operation and doing a large business in Canada, Europe and the United States; the demand for the company's products in Canada is not sufficient, hence the European and American exports. The present products are pitch and the various grades of benzol, creosote-oil and carbolic acid.[35] Large extensions are looked for from this company, which will be guided by the motto *festina lente*, and as opportunity offers, will branch into the production of other commercial commodities arising out of coal-tar and its distillation products.

ASPHALT.

Asphalt occurs naturally in several varieties as albertite, found in King's and Albert Counties, N.B., and as maltha, one of the stiffer petroleum compounds, which is not of much importance however, being almost too hard for use in street paving. Up to 1898, albertite was employed in gas-making, and much of it was shipped to the United states; but the original supply is now exhausted.

IX.—CALCIUM CARBIDE, CARBORUNDUM, CORUNDUM, AND GRAPHITE.

CALCIUM CARBIDE.

The production of this substance on a manufacturing scale dates back only to the year 1891, when Mr. T. L. Willson, of the Willson Aluminum

(34) Inland Revenue Bulletin, No. 81, 1902.
(35) Letter from Mr. John Craven, Sydney, 2nd Feb., 1905.

Works, at Spray, N.C., accidentally obtained carbide whilst trying to reduce lime by carbon in the electric furnace. Instead of metallic calcium resulting—which was to be employed in preparing aluminum—a hard, almost black, substance was got which reacted violently with water, giving lime and an inflammable gas clearly recognizable as acetylene. The author was privileged, through the courtesy of Lord Kelvin, to have at one time in his possession some pieces of the first carbide made by Mr. Willson at Spray. Acetylene being a powerful illuminating agent and readily obtained from carbide, the development of the carbide industry on a commercial scale followed this discovery as a natural consequence. The industry has progressed by leaps and bounds during the past decade, in Europe even to the extent of over-production.[36] Two carbide works are in operation in Canada using water as their source of power, the Ottawa Carbide Company, and another important company is the Shawinigan Carbide Company of Shawinigan Falls, Quebec. The process of manufacturing consists in fusing together burned lime and ground coke in the electric furnace; the temperature required is not so high as that needed in other operations for which the electric furnace is employed, notably the making of carborundum and graphite. The reaction taking place in the furnace results in a transference of the oxygen of the lime to a portion of the carbon with the formation of carbon monoxide and carbide of calcium.

The present market value of carbide affords considerable profit to its manufacturers, and the increasing popularity of acetylene as an illuminant ensures a brighter future for the industry. In Ontario several towns have already had acetylene installed for house and street lighting, the gas being generated at a central station and distributed in pipes to the consumers.[37] At the generating station the gas is purified by a special process before use, which obviates all the disadvantages inseparable from the employment of small generators—automatic or otherwise—by individuals, who in most cases have neither the time nor the scientific skill necessary for the proper production of the gas, simple as it may appear at first sight.

CARBORUNDUM.

Ten years ago the very name "carborundum" was unknown; it is due entirely to the advance made in the development of electrical power, obtained from the immense waterfalls of the American continent, that this as well as other materials are now in daily use throughout the world.

(36) Italy alone possesses enough carbide plants to supply the whole of Europe. Dr. J. W Richards, in "Electro-chemical Industry." Sept. 1902.

(37) Worked under patents held by the Burgess Gas Process Co., Canadian Pat. 73,040 Sept. 10 1901; Eng. Pat. 241, Jan. 3, 1901; Amer. Pat. 701,995, June 10, 1902.

The history of carborundum, may well be likened to that of carbide, its discovery being accidental. Mr. E. C. Acheson, whose patents are employed in this industry, was endeavouring to obtain crystals of carbon by melting together clay and carbon, the latter of which it was hoped might crystallize from the resulting reduced aluminum. Hard crystals were found after the fused mass had cooled, the component parts of which were concluded to be carbon and aluminum, and for which he invented the name "carborundum." Analysis, however, proved the new substance to contain silicon and carbon, and only a small quantity of alumina. Further experiments were made with mixtures of sand, carbon and salt as a fluxing agent, and large crystalline masses of carborundum were obtained. The substance thus formed corresponds to the formula CSi, is extremely hard, and is used in place of emery and corundum. In the manufacturing process the materials employed are sand, coke, salt, and sawdust; the coke is reduced to kernels of a certain size, to be used for making the "core," and other portions are ground to a fine powder for mixing with the charge of sand and salt. The original form of furnace was fitted with a pair of carbon terminals, which could be moved longitudinally, and was essentially an arc furnace, the chemical changes taking place being due to the high temperature of the arc passing between the carbon terminals. In 1895 this form was abandoned and a continuous electrical connection made between the terminals by the introduction of a "core" of granulated coke. By regulating the diameter of the core it could be heated to a sufficiently high temperature to convert the surrounding mixtures into carborundum. In the modern form of furnace the brick ends and carbon electrodes, with the necessary terminals for connecting up the current, are the only permanent portions. The charge, consisting of sand, finely-ground coke, and sawdust,—added to render the mixture more porous and consequently allow the gaseous products to pass through the mass—is placed in the furnace till it is on a level with the lower edge of the carbon electrodes. The coke "core " is then filled in, made into cylindrical form by hand, and finally surrounded at its sides and on the top by the remainder of the charge. Care is taken to prevent the mixture coming in contact with the carbon terminals, and necessary retaining walls are built up of bricks as the charging operation is proceeded with. The current is passed for thirty-six hours, and after cooling, the walls are taken down, unused "charge" raked off, and the outer crust of carborundum exposed. A cross section of the contents of the furnace presents many interesting characteristics. In the centre is the core, which has been, to a large extent, converted into amorphous carbon and graphite. From this there radiate beautifully coloured carborundum crystals to a distance of from ten to twelve inches. Next a thin inner crust of amorphous carborundum of a light green colour is met with, then the outer crust, also

amorphous, and beyond this, the unchanged mixture.[38] A curious effect is observed near the core, where the temperature is highest; here are found crystals of carborundum, from which the intense heat has volatilized the silicon, leaving "skeleton" crystals of graphite, while the silicon, passing outwards oxidizes to silica, and often presents the appearance of spun glass. Silicon itself has been found in the cracks in the bed of the furnace.[39] The carborundum is finally crushed, washed, and graded for the market.

Carborundum has a lower specific gravity than emery, and finds its principal application in the manufacture of wheels, stones, razor hones, rubbing bricks for marble dressing, paper, and cloth. The Canadian works of the Carborundum Company were destroyed by fire in 1903 and have not been re-built. This plant was comparatively small, only operating 200 horse-power. The factory, however, supplied the Canadian market, thus avoiding the payment of duty. The writer was informed by Mr. Acheson that most of the Canadian product was exported to Scotland, to be used there in finishing granite. The estimated cost of the crude crystals is 2.5 cents per pound, that of the treated powder, 4.5 cents per pound, while the selling price averages 9 cents per pound.

CORUNDUM.

The natural corundum industry of Ontario, which is of recent origin, is, however, now steadily growing in amount and value of output. The production of corundum in 1901 had a value of $53,115, and in 1903, $106,332, and in 1904 over $3,000,000.[40] The chief producing company, the Canada Corundum Company, has just completed a new mill of greatly enlarged capacity, and the other operating concern, which formerly exported the corundum-bearing rock to the United States, after cobbing it merely, is now crushing and treating it on the spot. Two additional companies are in process of organization for producing corundum.[41]

To the Canada Corundum Company, of which Mr. B. A. C. Craig is the president, may be accorded the credit of having placed the natural corundum industry of Ontario on a firm basis. Craig Mountain is said to be the largest deposit of corundum in the world. The hardness of this substance has long been known, and under the name of emery it has, in an impure state, been used as an abrasive agent. The product of this mine is said to contain from 95 per cent. to 98 per cent. crystalline alumina, and from letters the writer has seen, its hardness and cutting qualities seem

(38) Illustrated Catalogue No. III., Carborundum Company, N.Y.
(39) Electro-Chemical Industry, Vol. I., No. 2.
(40) Letter from Mr. B. A. C. Craig, President of the Canada Corundum Company.
(41) See 19 *bis*.

to have recommended it to consumers alike in Europe and on the American continent. Results are always the best tests of the efficiency of any agent, and the rapidly increasing market that Ontario's corundum is finding is sufficient evidence of the quality of this material. The Craig Mine is now putting out about ten tons a day, and the management confidently expect a considerable increase in the spring.[42]

GRAPHITE.

Though no company for the manufacture of graphite has yet been capitalized in Canada, the production of it by the Acheson process is carried on to a small extent in the Canadian branch of the Carborundum Company at Niagara Falls. The formation of the "skeleton" crystals referred to above suggested making use of the decomposition of carborundum for making graphite itself. The inventor's patents include the production of graphite in the form of pure electric-light carbon, by subjecting impure carbon to a high temperature for a sufficient length of time to volatilize the impurities;[43] the conversion of carbon into graphite by mixing with such metallic oxides as would be capable of forming metallic carbides, to be subsequently decomposed;[44] the conversion into graphite of such natural carbonaceous materials as contain uniformly intermixed through them metallic oxides sufficient to produce carbide, and thence graphite.[45] These processes throw considerable light on the scientifie principles underlying the formation of this substance.[46]

X.—THE CEMENT AND PLASTER INDUSTRY.

The manufacture of Portland cement is mainly confined to Ontario, though one establishment—the Crescent Cement Works—is situated at Longue Pointe, in the Province of Quebec. In Ontario there are some fourteen companies and eight factories in operation, and throughout this Province are found the necessary raw materials (clay and marl) of an excellent quality. The development of the industry has been rapid, and has all taken place within the past few years. The most improved method of procedure is as follows: the marl is thoroughly mixed, mechanically, with water into a thin paste, and the same operation is performed with the clay. The two fluids are mixed thoroughly in the required proportions, and in a pasty condition are pumped into steel rotary calciners, about seventy feet in length and six feet in diameter, set at a slight angle to the

(42) See note 40. An account of the Corundum Industry of Ontario will be found in the "Canadian Mining Review," Vol. XXIII, No. 10, (1904).

(43) U.S. Pat. 542,982 of July 23, 1895.

(44) U.S. Pat. 568,323 of Sept. 29, 1896, and No. 617,979 of Jan. 17, 1899.

(45) U.S. Pat. 645,285 of March 13, 1900.

(46) Electro Chemical Industry, Vol. I., No. 2.

horizontal. These rotary calciners are the great feature of the Canadian cement plants. This form of kiln is originally of English origin, but has only been brought to its present effective condition since its introduction to this country. In the interior of the kiln are "channel-irons" running from end to end. At the lower end fuel is introduced in a particular manner, and the burning gases pass through the entire length of the kiln, and are allowed to escape at the upper extremity. At this latter end is introduced the "slurry" of the mixed ingredients, which becomes dried and finally calcined in the slow passage from one end to the other. The revolving irons carry the "slurry" up with them as they rise, and on reaching the top it falls, under the action of gravity, through the burning gases, being subjected at the hottest part to a temperature of 3,000° F., when combination takes place between the constituents of the fused mass, and the resulting "clinker" emerges into the vessel destined for its reception. The drying and calcining is thus performed in one operation, and no preliminary pressing of the material into bricks is required.[47] At the works of the National Portland Cement Company, recently erected at Durham, Ont., a great saving of time is effected by cooling the clinker in vessels drawn by an endless chain through a stream of water below the ground level. After cooling in this manner it is ground to a fine powder, and packed in bags or barrels ready for use. The whole operation by this process occupies only eight hours, a period of time which will be appreciated by all acquainted with the older methods. At Durham the raw materials are brought from the natural deposits, which are close at hand, calcined, cooled, ground and packed by means of a continuous series of mechanical conveyers from one part of the establishment to the other. This company has another plant in course of erection at Hull, P.Q., on the Ottawa River, which is intended to supply the Eastern Canadian market.

Several articles have appeared lately in the public press[48] pointing out that a possible over-production of cement may be the result of the numerous large concerns which are already in operation or are about to be started. Whether or not this will take place in the immediate future depends, naturally, on the general prosperity of the country and the consequent demand for building materials. Certainly cement has gained considerable reputation as a substitute for stone, as can be seen by the extent to which it is made use of by architects. It can be readily moulded into any form and may then be dressed to represent the natural article. If it can ever oust stone and brick from their present position depends, not only on its comparative cost, but on the quality of cement put out by manufacturers. One case of a collapse due to an admixture of a single bag of inferior material and the whole fabric of the cement industry

(47) The Portland Cement Industry: "Queen's Quarterly," Jan. 1903.
(48) "*The Globe*," Toronto, March, 1903, and other papers.

as supplying a substitute for the older building materials, will be in danger of a similar fate. The total output of Portland cement in 1902 was valued at 1,028,618 dols.,[49] and in 1903 at 1,166,497 dols.[50]

Gypsum is found in considerable quantities in Nova Scotia and New Brunswick. At Windsor, N.S., there are immense deposits; the beds found in the vicinity of Hillsborough, N.B., are, however, very large and of great purity, and form the basis of the most extensive operations.[51] It is also found in Ontario, and plaster works are located at Paris in that Province. In 1901 active operations were begun at Gypsumville, Manitoba. The industry, however is principally located in New Brunswick. Drawbacks in the way of freight charges, inadequate shipping facilities, and the competition offered by manufacturers of plaster of Paris in the United States, kept the industry from developing until the Intercolonial Railway was opened and the increased duty on American plaster imposed, when the New Brunswick plaster, quarried and prepared at Hillsborough, came to be firmly established on the Canadian Market. In manufacturing plaster of Paris, the stone is first dried in the air and ground—not burned in lumps as is still done to a considerable extent in England and on the Continent of Europe, and the pulverized material subjected to a process of calcination in kettles, of a capacity of sixty barrels of 300 pounds of the calcined plaster, furnished with lids and stirring arms which keep the material in constant motion. When the required temperature has been reached (285° F.), the plaster is removed and packed in paper-lined barrels for market. Analysis of the Hillsborough gypsum shows it to be 99.88 per cent. $CaSO_4$.[52] The principal markets for plaster of Paris are Canada, the United States, and South Africa, while the crude gypsum is exported largely to New York and other portions of the States, being used for making plaster for walls and ceilings.[53] According to the Geological Survey Reports for 1902, the gypsum produced in Canada during that year amounted to over 332,000 tons, valued at 356,317 dols.

XI.—CARBOHYDRATES: (A) THE REFINING OF SUGAR; (B) THE BEET-SUGAR INDUSTRY.

The hoped-for developments in the production of sugar from beets in Ontario and Southern Alberta, referred to in the first edition of this paper (1903) have not come up to the expectations either of the writer or of the public as will be seen from the sequel. Statistics show that during

(49) Geological Survey of Canada: Mineral Products, 1902.

(50) Stattisical Year Book, 1903.

(51) Geological Survey of Canada: The Mineral Resources of New Brunswick, 1899.

(52) Analysis by A. A. Breneman, of New York, in Mineral Resources of New Brunswick, Geological Survey of Canada, 1899.

(53) Letter from the Manager, Albert Manufacturing Co.

the last decade cane sugar has increased in production about 200 per cent. Judging from present appearances, and allowing for some slight tariff alterations, the increase in Canada should soon be in proportion to that of other countries.[54]

Raw sugar is imported from Cuba, the West Indies, Java, Manila, the Brazils, Mauritius, and the Continent of Europe. The most improved machinery and processes are employed, refined sugars and syrups being the staple products,

Belgium supplies to Canada the largest proportion of sugar, the imports from that country amounting in 1901 to 127,931,553 pounds; from Germany in the same year 83,941,290 pounds entered the country, the total imports being 336,694,833 pounds valued at close on $8,000,000.[55]

BEET SUGAR.

The most interesting point connected with the sugar industry is the way in which the production of sugar from beets cultivated on Canadian soil has become, in the past few years, an important factor in the country's progress. As far back as 1872 the Dominion Government sent a special agent to Europe to make a study of the industry. A bounty of $25,000 afterwards increased to $70,000 was offered by the Quebec Government in 1875 to the first successful factory to be established in a situation approved by the Government. This led to the establishment of a company known as the Union Sucriere du Canada, which, in 1881, erected the first of four proposed factories at Berthierville, Que.[56] This establishment was unsuccessful and only operated for a few days, mainly owing to the failure of the beet crop. After passing into other hands the plant was bought by an American company and removed to Eddy, New Mexico.[57] Another company was, in the same year, organized at Farnham, P.Q., not far from Montreal, which after some vicissitudes, did not deem its success sufficient to warrant a continuation of its operations, so sold its plant to a company at Rome, N.Y., in 1897. A third company, known as the Pioneer Beet Company started operations in 1881, at Coaticook, P.Q.,[59] and was successful in part, receiving a subsidy of 35,000 dols. from the Government, but it, too, closed its doors in 1883. The causes to which these failures may be attributed were lack of capital and enterprise, and the indisposition of the farmers to cultivate beets. The Agricultural Department of the Provincial Governments, however, continued experimenting with various kinds of beets and studied the conditions most favour-

(54) Letter from Mr. D. A. Gordon, President of the Wallaceburg Sugar Company.
(55) Essay, Mr. Read, University of Toronto.
(56) Report of Dominion Government on beet sugar manufacture in Canada.
(57) Letter from the Manager of the Dresden Sugar Co., Ontario, now removed to Michigan.

able to their successful growth. For some years past the Ontario Agricultural College at Guelph has, as a consequence of the excellent results obtained at their experimental stations, been carrying on an educational campaign among the farmers of the Province. As a result of this the quality and tonnage of beets now grown in different parts of Ontario surpass those of many American States. The climate of this Province, with its sunshine and long autumns, is peculiarly favorable to the cultivation of the beet, which takes about four months and a half to reach maturity. It requires, however, to be demonstrated to the farmers that the cultivation of beets will pay them better than other land produce before the requisite supply of suitable material will be obtained. That the profits are large can be gathered from the fact that wheat yields in Ontario $15 an acre per annum, oats, $9.74, and beets for sugar, $60. In the last case the cost of production is necessarily large, owing to a great amount of labour being required, but, all the same the profits to the farmer should, with skilful treatment, be at least $30 per acre per annum. The beet tops are of value as a fertilizing agent owing to the salts they contain, and find a use also as a food for cattle. In 1901 beets were grown —under instructions from the Agricultural Department—in fifteen districts of Ontario, and the average yield per acre was over seventeen tons of a high quality of beets which gave an average of 15.6 per cent. of sugar of an average purity of 87.7 per cent. All this points to a future for Ontario as a sugar-producing country; this fact has been fully realized by the Provincial Government, which offered a bounty of $275,000 for three years,[58] and at its recent session extended this bounty for a further period of two years, to be distributed among factories according to the amount produced. Four companies were organized a few years ago, namely, the Wiarton Beet Sugar Company (capital $500,000) which has since been shut down; the Dresden Sugar Company (capital $600,000) which has now removed its factory to Michigan; the Wallaceburg Sugar Company (capital $500,000) and the Ontario Sugar Company, of Berlin (capital $1,000,000); each of these companies received a bonus from the town where it was situated, averaging $28,000. The capitalization of a company engaged in this industry depends entirely on the size of the plant, a general estimate of $1,000 per ton of beets per day may be considered a fair calculation of what would be required.

Two companies only are thus in the field this year, and it seems reasonable to expect that both factories will increase their output over that of 1903. The nearness, geographically speaking, of the Wallaceburg and Dresden concerns to one another—some nine miles apart only—militated against their success, and it is to be hoped that now the former is, so to speak, alone, it will do better than heretofore.

(58) 1, Edw. VII., Cap. II, (1901).

Beet sugar factories have also been established in Alberta, in the North-West Territories of Canada. Since 1893, an area of about 300,000 acres has been made productive by means of the irrigation system of the Canadian North-West Irrigation Company, and a portion of this area has been utilized for beet cultivation, principally by the Mormon settlers. The most important factory has been established by the Knight Sugar Company at Raymond, south of Lethbridge, on the Canadian Pacific Railway. The capital of this company is $1,000,000. The area intended to be planted with beets is 3,000 acres, and the daily capacity of the factory will be 400 tons of beets per day. The only difficulty which the industry is encountering in the North-West is the scarcity of labour.[59] This is due partly to the scanty settlement of the country, and partly to the superior attractions of the mining regions, which are situated at no great distance.

A plentiful water supply, lime, and source of power, are necessary for the profitable prosecution of the industry; all this has been carefully considered in locating the factories enumerated above, steam power being employed for pumping and the working of all machinery. There is room for many more factories in the Dominion; according to Dr. A. B. Shuttleworth, Chief Agriculturalist to the Ontario Sugar Company, whose name is indissolubly connected with the development of beet cultivation, it would require over thirty refineries each of 600 tons capacity to supply the home market alone.[60]

The working season of a factory runs for about 100 days, operating continuously. The cost of the sugar is from three to three and a half cents per pound, and the profits to the makers are estimated at fifty cents per ton of beets used. This would mean that in a factory of 500 tons capacity, working for 100 days, the profits would amount to $25,000.

The scope of this article does not allow of any detailed consideration of the working process by which the sugar is extracted frm the sliced beets and crystalized. New proceses are being employed for utilizing the residual molasses. This is treated for the recovery of the sugar in some part, and also for the production of alcohol by fermentation. An American company in 1901 produced 915,000 gallons of alcohol in this way, of a quality considered to be quite equal to the grain product. Another new process is that of the manufacture of syrup from the beet instead of sugar; forty gallons of this can be obtained from a ton of beets, which, at thirty cents a gallon, means a return of $12 per ton of material used, while the product in sugar yields only from $7 to $8 per ton of beets. The

(59) Letter from Manager of works at Raymond.
(60) Berlin News Record, Nov. 8, 1902.

beet-pulp refuse is also being largely used as a food for live stock, for which purpose it is extremely suitable owing to its nitrogen contents. In this connection a new process has been introduced for drying the pulp, which entails an expenditure of $5 per ton, but, as the dried pulp is sold at $6.25 per ton, a clear profit of $1.25 is thus secured to the manufacturer.[61]

The production of sugar from Canadian grown beets is a new and, it is to be hoped, rising industry which offers great scope for some co-operative arrangements between the companies and the farmers. It should give an impetus to agriculture, afford employment to thousands of unskilled workpeople, and, as an important industry, be a lasting benefit to the country. Whether or not the growing of beets will become popular remains to be seen; the present quality is as yet not so good as was expected, but much may yet be done in the way of improvement by careful cultivation.

The following communication, dated March 6th, 1903, from Mr. George Elsey, manager of the Dresden Sugar Company, conveys some idea of the position of the industry from the point of view of the manufacturer and its possible future:

"At the present time there were four factories which operated this last season, and from what we are able to learn the results were as satisfactory as could be expected under the existing conditions, that is, the rain fall last summer damaged the beet crop from fifty to sixty per cent., both in the United States and in Canada. The balance of the crop, on account of wet weather, cost considerably more to raise than what was necessary. It was unfortunate that this should occur in the first season that the factories were started in Canada, as it was very disappointing, but most of the farmers have told us that they were surprised at the amount of rain the beet would stand, and in several instances where they could harvest the beet crop, the corn and other crops were ruined. After we have had a seasonable year and it will be demonstrated to the farmers that there is more money in raising sugar beets than any other crop that grows, the four factories now in existence will get their supply of beets within hauling distance of the factories. . . . Our farmers know well that the Michigan farmers obtain about a dollar a ton more for their beets than they do, and they also understand that it has cost as much in money and labour to raise a ton of beets in Canada as it does in Michigan or any part of the United States. They therefore feel dissatisfied, and are clamouring for more money, which the companies would be glad to pay if they could sell their sugar for the same price as the American Beet Sugar refineries. The present Canadian sugar tariff is such that it would not allow any

(61) In the above I have drawn largely from an essay on the beet-sugar industry by Mr. E. R. Read, a student in the Department of Political Science, University of Toronto, who kindly placed his papers at my disposal. Also from Dr. Shuttleworth's article in the "*Berlin News Record*," 1902.

more sugar refineries to be built in Canada. The companies that are already here have the experience of what this tariff can do. It allows sugar that has been refined in the United States to be shipped in here and undersell Canadian refined sugar, which means a loss to the refineries and to the Canadian people. It allows raw beet sugar to be imported at a price that will prevent the farmers from taking hold of the beet industry as they should. Canada is sending to Germany and other foreign countries about $1,000,000 per month for raw beet sugar, and the naturally yearly increase of consumption is about eight per cent, so that the future of the sugar beet industry, under a proper tariff, would be a lasting one and a great benefit to the farming community."

XII.—NATURAL GAS AND PETROLEUM.

NATURAL GAS.

The existence of natural gas in Ontario was first discovered in 1889, being found in two well-defined areas, as the Essex county field and the Welland county field. It is chiefly near Buffalo, on Lake Erie, and near Windsor, Ontario, that the largest supplies are met with, though practically it may be got in nearly any part of the Niagara peninsula in small quantities. In 1901 there were 158 wells in operation, and 368 miles of piping were needed to distribute the gas. Much of the gas produced in Essex county was formerly led across the river to Detroit by pipe lines, but on representations made by the people of the Essex district to the effect that the supply of gas was not sufficient for home consumption, the Ontario Government passed an Order in Council in October, 1901, prohibiting the gas from the Essex field being exported to the States. None of the product of this natural gas field is therefore now being sent across the Detroit river; it is, however, still exported from the Welland field to the American side of the Niagara River, chiefly to Buffalo, N.Y. It may be mentioned that the landowners on whose farms the wells are located get their gas free in addition to being paid for the use of their lands.[62] The value of the gas produced in Ontario during the last ten years shows considerable fluctuations, being much less in 1903 than in the previous year, due, no doubt, to the Government prohibiting its export.[63]

PETROLEUM.

This is one of the chief mineral products of the Dominion, though as yet the output is not sufficient to meet Canada's needs. The principal seat of the industry is at present in Ontario, where commercial quantities

(62) Report of the Bureau of Mines, Ontario, 1902.
(63) Statistical Year Book of Canada, 1903.

are found in the counties of Kent and Lambton. In the former there are two oil fields, one at Oil Springs, extending over 1,200 acres, and the other in the Petrolea district, 20 miles long by 2 wide.[64] In Lambton county the industry dates back to the year 1862. Petroleum is also found in Quebec, Nova Scotia, New Brunswick, and boring operations that have in recent years been carried on at Athabasca, near Edmonton, in the North-West Territories, point to a likelihood of that part of the country contributing largely to the future supply of mineral oil.

The industry is now one of the most highly organized in the Dominion; the system of drilling and pumping now used—the "jerker-line" system enables a well yielding from eight to ten gallons a day to be profitably worked. This system has gained for itself a world-wide reputation; it is used in Galicia, Russia, Afghanistan, Burmah, India, Italy, France, California, and Australia. Its advantages are numerous; a central engine can operate a large number of wells; on one property near Petrolea, 233 wells, scattered over an area of 400 acres, are worked by a single engine. It is estimated that to sink a well of about 500 feet in depth costs only $125.[65] In 1900, there were approximately 10,000 wells in operation, yielding on an average seventy-one barrels of oil each.

The refining side of the petroleum industry is largely in the hands of the Imperial Oil Company,[66] which some years ago absorbed several other concerns, and of the Canadian Oil Refining Company. The plant of the former at Sarnia has a capacity of 60,000 barrels of crude oil per month, and the market for their products reaches from Halifax to Vancouver. Many of the bye-products of the refining process find a market in England and in Spain. The latter company have erected an up-to date plant at Petrolea, on the site of one which was in operation some years ago, where all the products will be manufactured that modern science shows can be obtained from petroleum.[67] Improvements in methods of retorting have recently led to considerable quantity of the crude oil being used for gas making, three and a half million gallons being an estimate of the amount so employed.[67]

There has been a slight falling off in the production of oil during the past years; calculated as "crude" oil, the output in 1901 was 27 millions Imperial gallons, and in 1901 a little over 26½ millions.[68] In 1903 it fell to some 16 million gallons. A slow process of diminution seems to be going on in the area at present productive, and a falling off must be looked for

(64) The oil is found at depths varying from 370 to 400 feet.

(65) This and much of what is given here on natural gas and petroleum is from a paper by Mr. W. J. K. Vanston, read before the Canadian Section of the Society of Chemical Industry in Jan. 1903.

(66) Capital stock, $1,000,000.

(67) Bureau of Mines Report, Ontario, 1902.

(68) Statistical Year Book, 1903.

from year to year unless this is counteracted by an extension of the oil-bearing territories.[67] Probably, the field about to be exploited in the North-West will alter the position somewhat, and an increase in the output may be confidently looked for.[69]

XIII.—PULP AND PAPER.

PULP.

As timber is one of the chief natural products of the Dominion, it is only to be expected that Canada should figure largely in the wood pulp industry; the figures that might be given to indicate the number of cords of pulp-wood available throughout the country are so large that one could hardly grasp their real significance. The industry is not so young as many others that have been considered; in the census of 1871, no pulp-making plants are mentioned; in 1881, there appear five mills, employing 68 men, and having an output valued at $63,000; in 1891 there were 24, with a yield valued at more than a million dollars; while 1903 shows some 39 factories, from which the exported pulp alone amounted to over five million dollars.[70] The area of pulp-making operations is not confined to any one Province, New Brunswick, Nova Scotia, Quebec, Ontario, and British Columbia are all represented in the industry.

The principal woods employed for pulp-making are white and black spruce, balsam, poplar, and pine; spruce[71] and balsam are those most generally used, on account of the special quality of their fibre and their colour, pine being utilized mostly for chemical pulp. The two main varieties of the pulp are *mechanical* and *chemical*. The former is obtained by grinding spruce logs to powder, the logs being pressed against a rapidly revolving grindstone, with water constantly supplied to prevent the friction causing a rise in temperature. A liquid pulp is thus obtained from which the water is squeezed by hydraulic machinery, a pressure of many tons to the square inch being employed. The resulting pulp still contains water, however, to the extent of from 50 to 60 per cent., though some works—notably those at Sault Ste. Marie—have introduced a machine specially constructed for the purpose of removing this large excess of moisture. Where the pulp is to be made at once into paper, this drying process is unnecessary. The specially dried pulp resembles paper very closely in outward appearance.[72] Chemical pulp is prepared by disintegrating and

(69) Total value of products of petroleum in Ontario in 1901, $1,467,940, Bureau of Mines Report 1902.

(70) Statistical Year Book, 1903.

(71) In 1894 it was estimated that Canada contained between 38 and 40 per cent. of woodlands and forests, or about 1,400,000 square miles, one-half of this being spruce. The spruce area is thus 450 million acres. In all there are 4,500 million tons of pulpwood in sight. "Pulpwood of Canada." Pan-American Exhibition pamphlet, published by the Geological Survey, 1901.

(72) The Sault Ste. Marie Works used (1903) some 200 tons of spruce logs yielding 150 tons of pulp per day.

extracting the resinous matter from the wood —in the form of chips— by digestion with sulphur compounds, usually a weak solution of sulphurous acid, about a quarter of which is in the form of bisulphite of lime.[73] A soda chemical process is also employed by some makers. The sulphur used for the production of sulphurous acid is either imported from Sicily or obtained by burning pyrites. Chemical pulp possesses many advantages over mechanical pulp, though its manufacture is necessarily more expensive, and the yield per cord of wood, as compared with the latter, is much less.[74] It has a longer and tougher fibre, and the resinous matter being no longer contained in it, finds uses for qualities of paper for which the mechanical pulp would be unsuitable. The principal markets for pulp are Great Britain, the United States, France, Australia, and Japan. Much of it is used, however, locally for the manufacture of paper. In 1903 the requirements of Great Britain alone amounted to $12,000,000, a little over seven per cent. of her needs.

PAPER.

In many cases the producers of pulp also manufacture it into paper. The principal requisites for the paper industry are a plentiful supply of pulp-wood, good water and an abundance of it, and cheap power; all these can be found in many parts of Canada. The growth in the demand for paper of all kinds, news, wrapping, wall and the finer grades, was one of the features of last century—especially newspaper. The introduction of wood fibre into its manufacture has consequently enabled the supply to keep pace with the demand. The process of manufacture requires no description here; the secretary to a prominent Canadian firm states that originally they used rope as a raw material, then straw, which was abandoned for rags, and finally these gave place to chemical and ground wood-pulp. Previous to 1870 no wood whatever was used in the manufacture of paper in this country. Ground wood-pulp was introduced at that time and has since become the filling material of the cheaper grades of paper, being partly pasty and partly fibrous. Up to 1885 the real fibre—the framework of the paper —was supplied by rags. In 1885 sulphite pulp was introduced and has largely replaced rags, except in the higher grades of paper, in which linen is used, and in the very low grades, where straw is employed.[75]

The *Toronto Globe* of March 4th, 1903, in an article on the wood-pulp industry, gives the following statistics, which are of interest:—

	Tons.
Production of mechanical pulp in 1902	152,210
Production of sulphite pulp in 1902	76,735
Production of soda pulp in 1902	9,044

(73) Letter from Mr. Carl Riordan, Merritton, Ont.

(74) One ton of mechanical pulp requires a little over a cord of wood; one ton of chemical pulp requires a little over two cords of wood.

(75) Mines Report, P.Q., 1901.

XIV.—ASBESTOS AND MICA.

ASBESTOS.

This mineral occurs in large deposits in the "Eastern Townships" of Quebec, where it was first worked in 1878; from 1880 up to the present date the production of asbestos has increased steadily; the output that year is given as 380 tons, while in 1901 over 38,000 tons are recorded in the returns furnished by the producers. The world's supply of asbestos is, for the most part, obtained from Canada, and the Quebec deposits have in the past proved to be the most profitable mineral mined in the province. Thirteen mining companies are at work in this industry, which is principally carried on at Thetford, Lac Noir, and Danville, giving employment to approximately 1,000 men. Asbestos is shipped largely to Great Britain, the United States, Belgium, Germany and France.

MICA.

Another silicate found in Canada is mica, which, though occurring in small quantities, is a not unimportant industry; in Ontario there are several mines and a number of works where splitting, trimming, and sorting the material into saleable sizes is carried on. The Provinces of Ontario and Quebec produce the greater part of the mica used in the manufacture of electrical apparatus in the United States, and also export not inconsiderable quantities to Great Britain. The so-called "amber" mica, or phlogopite, is preferred for this use to other yarieties on account of its superior flexibility and the thinness of the sheets into which it can be split. The mica mines of the General Electric Company in Ontario produce large quantities of mica annually, and the Company have trimming works at Sydenham and Perth. There are also important mica trimming plants in Kingston and Ottawa.[76]

CONCLUSION.

The new Canadian Niagara Power Company, whose works are in the course of construction at Niagara Falls should give a fresh impetus to the development of industrial chemistry locally. This will be the first company to produce power on the Canadian side of the Falls. A feature in the plant is the size of the generating units, each of which will have a capacity of 10,000 horse-power. They will be more economical than generators of 5,000 horse-hower, will occupy but little more space and their cost will be much less per horse-power in comparison. It is expected that the output of the company will be used principally for Canadian industries and for such public utilities in the Province of Ontario as may be within reach of long-

(76) Letter from Mr. Thos. W. Gibson, Director of Bureau of Mines, Ontario.

distance transmission. The power on the American side is employed by some twenty or thirty firms engaged in such chemical industries as the manufacture of pulp and paper, silver plated goods, chlorate of potash, caustic alkali, salts of tin, carborundum, carbide, graphite, pure metallic lead, "alundum"—another emery substitute,—cereal food-stuffs, nitric acid and composite boards made from wood-pulp and flax-fibre. Judging from all this there should be a large increase in the number of chemical industries in this neighbourhood when the Canadian power station is completed and the current available from the Falls to Toronto.

The subjects that have been considered in this paper do not by any means exhaust the catalogue of chemical industries in Canada. Many important manufactures have, for the reasons mentioned in the opening paragraph, been omitted. A short summary of these will suffice. Matches, for example, constitute an important and necessary article of daily use, and are made in enormous quantities, practically all that are used in Canada being manufactured in the country. Brewing and distilling are carried on extensively also, ale, lager beer, and stout being made, while Canadian rye whisky is known throughout the whole English speaking world; even a "Canadian Scotch" is produced at Perth, Ont.; brandy and champagne and other wines are made at Hamilton, Brantford, and Pelee Island, on Lake Erie. Fruit canning is one of the great industries of Wentworth and Essex Counties, Ont.; bacon packing and salmon canning may also be classed among those manufactures requiring the careful supervision of the skilled chemist. To the list may be added explosives of all kinds; blackings, varnishes, japans, lacquers, paints and shellac, foodstuffs and sauces; antitoxines for use in the practice of medicine are made by the Parke Davis Co. at Walkerville. Natural mineral waters are abundant, at St. Catherines, in British Columbia and in Quebec, while manufactured aerated waters are made in mostly all the important towns. The almost universal wearing of india rubber foot coverings during the winter season necessitates the production of large quantities of goods of this sort. Many large factories for this purpose are in existence from which rubber goods of a superior quality emanate; dyeing and calico-printing might also be mentioned as being in a flourishing condition. The attitude of manufacturers towards chemists has of late years been extremely favourable, and many have seen it to be to their advantage to employ men trained in our universities to investigate the processes and materials employed in their particular industries. So far their employment has been amply justified by the results, and it is to be hoped that more may be brought to see the profit to be gained by adopting scientific methods of work. The university man who has specialized in chemistry can assist the manufacturers in this by bringing to bear on the *rationale* of the technical processes the general scientific knowledge which he

has gained during his college course, and his experience of methods of research and manipulation; he can thus materially benefit his employer by improving the quality of his products or enabling him to turn out his goods at a cheaper rate. Let the manufacturer, be he dyer, tanner, pulp-maker, or ironmaster, indicate only that he is willing to find employment for men educated in the higher branches of scientific work, and the universities of the Dominion will supply them. Where chemical processes are used, it is essential for the prosperity of this country that all the available scientific knowledge should be brought to bear on them, in order that they may continue to improve and to develop even more than they have done in the past decade. Canada, with its immense natural resources, and its water power should, in time and with proper management and assistance in the lines indicated, become one of the largest producers of the world's supplies.

In conclusion, I wish to acknowledge the great assistance I received in preparing the previous edition of this paper, from Mr. Fred P. Clappison, B.A., then Fellow in Political Science in the University of Toronto, who gathered together for me from all quarters much of the information required for this short and imperfect account of the chemical industries of the Dominion. In particular his help in connection with the statistics contained in the text and in the appendices was invaluable. Much of what appeared before has been repeated, though many alterations, omissions and additions have been necessary. To the gentlemen who so kindly answered enquiries as to their particular industries and placed valuable material at my disposal I desire also to convey my hearty thanks.

APPENDIX I.

THE IRON ORES OF CANADA.

Nova Scotia.—Magnetites in enormous quantities at Nictaux, in Annapolis County, at Whyhogomah, in Inverness County. Specular and red hæmatite at Nictaux, Stewiacke, Pictou, Antigonish, Guysboro, East Bay, and many other points. Limonite, specular, spathic clay ironstone and hæmatite at Londonderry. Mineral fuel and fluxes are in close proximity throughout the whole district.[77]

Cape Breton.—Extensive deposits of brown hæmatite, magnetite, and spathic ores lying adjacent to the great coal-fields.[78]

New Brunswick.—Magnetite and bog ores. Coalfields at Grand Lake and hardwood throughout the Province.

Province of Quebec.—Very extensive deposits of bog and lake ores, extending from the Province of Ontario to Gaspe, Magnetite deposits especially good at Sherbrooke, Leeds, Sutton, St. Jerome, and in Pontiac County. Hardwood and limestone abundant. Deposits of chrome-ironstone found in 1895 in Coleraine. The "Eastern Townships" obtain iron by dredging in the Lac-a-la-Tortue. Magnetites at Hull, near Ottawa.[79]

Ontario.—Vast deposits from the Ottawa Valley to head of Lake Superior, comprising magnetite, red hæmatite, limonite, specular, and occasional bog ores. The Helen Mine, at Michipicoten, is said to be one of the richest in the world. There are also extensive forests of hardwood, especially suited for the production of charcoal, and fluxes in abundance.[80]

Manitoba.—Magnetite, hæmatite, and bog ore on Lake Winnipeg. Hardwood in adundance.[81]

British Columbia.—Magnetic ores at Texada Island and Cherry Tree Bluff. Coal and wood in plenty. Collieries at Nanaimo (Naval coaling station for H. M.'s ships), Wellington, and Comox. A recent discovery of large deposits of magnetite has been reported in the Boundary Region, which at present mainly finds a use as a flux.[82]

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(77) Nova Scotia Report of Mines, 1901.
(78) Report of Geological Survey.
(79) Mines and Minerals of Quebec, Dept. of Mines.
(80) Bureau of Mines Report, Ontario, 1901.
(81) Geological Survey of Canada, 11th Annual Report.
(82) Geological Survey of Canada, 11th Annual Report

APPENDIX II.—METALLIC PRODUCTION OF CANADA, 1892-1903.

Metals.	Value, 1892.	Value, 1897.	Value, 1901.	Value, 1902.	Value, 1903. ‡
Pig Iron.....	637,421 dols	53,796 tons.	1,212,113 dols. †	1,043,007 dols.	707,838 dols.
Copper in Mattes.....	818,580 " *	1,501,660 dols. *	6,096,581 " †	4,511,383 "	5,728,261 "
Nickel in Mattes.	1,399,176 " *	1,399,179 "	4,594,523 " *	5,025,903 "	5,002,204 "
Arsenic.	1,000 "	.....	41,676 " †	48,000 "	15,420 "
Gold.....	907,601 "	6,190,000 "	24,128,503 " †	21,336,667 "	18,834,490 "
Silver	193,441 "	2,613,173 "	3,265,354 " †	2,238,351 "	1,170,779 "
Aluminum.....	.....	.....	1,000,000 "	1,643,250 "	.....
Lead.....	49,422 "	1,396,853 "	2,249,387 " †	934,095 "	762,660 "

* Value of metal if refined. † Statistical Year Book, 1903.

‡ Subject to revision, Mr. T. W. Gibson states that the total pig iron and steel produced in Ontario in 1903 amounted to 87,004 tons and 15,229 tons respectively; the whole of Canada yielded, during the same period, 265,418 tons of pig iron and 232,641 tons of steel.

APPENDIX III.‡—IRON AND STEEL PRODUCTION.

Company.	Plant at	Built.	Source of ore.	Employees, 1902.	Output in Tons.				Capacity of Furnaces in tons per day.		Capitalization.
					Pig Iron.			Steel.			
					1892.	1901.	1902.	1901.	1892.	1902.	
											Dols.
Canada Iron Furnace Co...	Midland, Ont....	1899	Ontario.....	..	..	18,948	..	..	..	..	1,000,000
	Radnor, Que.....	..	Quebec.....	..	5,574	31,159	..	..	40	..	..
	Londonderry, N.S.	1887	N.S.....	*	28,052	*	*	*	40,000 per ann.	150	..
Hamilton Steel & Iron Co.....	Hamilton, Ont....	1896	Ontario and U.S.A.....	1,000	† 1,000	..	51,701	9,473	†	..	1,500,000
Nova Scotia Steel and Iron Co....	New Glasgow, N.S.....	..	N.S..	965	29,502	28,407	..	23,916	100	100 pig, 100 steel	5,000,000
Deseronto IronCo.	Deseronto, Ont ..	..	U.S.A.....	..	..	13,701	..	..	..		..
Dominion Steel & Coal Co.....	Sydney, N.S.....	1901	Newfoundland.	6,000	†	27,643	191,259	86,424 (1902)	†	1,000 pig, 800 steel	33,000,000
John MacDougall and Co.....	Drummondville, Que.....	..	Quebec	..	..	793	..	..	6	..	..
Cramp Ontario Steel Co.....	Collingwood, Ont.	1900	Ontario and foreign....	†	..	..	..	..	..	200,000 per ann.	..
Lake Superior Power Co.....	Sault Ste. Marie.	1901	Ontario.....	500	..	..	..	..	†	..	117,000,000

* Not in operation, due to repairs being made. † Not in operation. ‡ Prepared by Mr. F. P. Clappison in 1903, largely from private letters.

APPENDIX IV.*—PORTLAND CEMENT AND PLASTER OF PARIS.

Firm or Company.	Place.	Capital.	Capacity of Plant in barrels per annum.	Output, 1902	Date of Beginning Manufacturing.
		Dols.			
Canadian Cement Co.....	Longue Pointe, Que....	200,000	....	....	....
Canadian Portland Cement Co.	Deseronto, Ont.....	1,500,000	250,000	250,000	1893
Lakefield "	Lakefield, Ont.....	590,000	75,000	75,000	1902
Imperial "	Owen Sound, Ont....	250,000	50,000	50,000	1902
Grey and Bruce "	" "	100,000	30,000	20,000	1902
Owen Sound "	Shallow Lake, Ont....	199,000	100,000	100,000	....
Sun "	Owen Sound, Ont....	500,000	40,000	40,000	1902
National "	Durham, Ont.	1,000,000	300,000	....	1903
Hanover "	Hanover, Ont.....	150,000	30,000	30,000	....
		4,399,000			
Albert Manufacturing Co., (Plaster of Paris).....	Hillsboro', N.B.....	350,000	....	60,000	....

* See Note ‡ in Appendix III.

APPENDIX V.—SUGAR FROM BEET ROOTS.

Company.	Place.	Capital.	Began.	Output.* July 02—July 03	Output.* July 03—July 04.	Capacity in tons of beets per day.
		Dols.				
†Wiarton Beet Sugar Co.....	Wiarton, Ont. ...	500,000	1901	1,565,000 lbs.	981,000 lbs.	350
Ontario Sugar Co.....	Berlin, Ont.....	1,000,000	"	6,063,926 "	7,059,695 "	600
‡Dresden Sugar Co.....	Dresden, Ont.....	600,000	"	3,763,987 "	2,094,999 "	600
Wallaceburg Sugar Co.....	Wallaceburg, Ont.	500,000	"	3,606,604 "	4,230,422 "	700
Knight Sugar Co.....	Raymond, N.W.T.	1,000,000	"	.....	.....	300

* Letter from Mr. C. C. James, Deputy Minister of Agriculture, Ontario. † Now closed down. ‡ Removed to Michigan.

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THE ACTION OF NITRATE OF SILVER ON DISODIUM ORTHOPHOSPHATE IN DILUTE SOLUTION.

BY WILLIAM ROBERT LANG AND WILLIAM PEROT KAUFMANN.

Received July 14, 1905.

THE generally accepted text-book expression for the reaction which takes place between solutions of disodium orthophosphate and nitrate of silver is given as being

(1) $\underbrace{Na_2HPO_4}_{142.1} + \underbrace{3AgNO_3}_{509} = Ag_3PO_4 + 2NaNO_3 + HNO_3.$

indicating the complete precipitation of phosphoric acid as a silver salt and the setting free of nitric acid.

From the molecular weight in (1) it will be seen that 1 gram of disodium orthophosphate should react with 3.57 grams of silver nitrate.

In order to determine the correctness of this expression, decinormal solutions of these were made up and the phosphate titrated with the silver nitrate, using potassium chromate as an outside indicator. As the result of from 200 to 300 determinations it was found that the "end-point" of the reaction, as indicated by the first appearance of the red silver chromate, invariably occurred when an amount of silver solution had been added corresponding to the proportion of 1 gram of disodium orthophosphate to only 1.447 grams of silver nitrate. These proportions would indicate that a reaction had taken place as expressed by the equation

(2) $2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3.$

Ostwald, in his "Scientific Foundations of Analytical Chemistry" (second English edition, 1900), on page 204, gives this equation (2) as being probably the more correct expression of the reaction taking place between these substances, but adds that, ".....it no doubt also fails to express all that goes on."

The analyses of types of the resulting silver phosphates may be tabulated as follows :

The figures in column (*e*) comparing the even with the odd, show that a greater yield of precipitate is obtained from the neutralized solutions than from those reacting acid, and a comparison of the yield of precipitate *obtained* and *calculated* in the

TABLE I.

a. Reaction of solution.	b. Grams Na_2HPO_4 used.	c. Grams $AgNO_3$ used when "end-point" with K_2CrO_4 was reached.	d. "End-point" overstepped.	e. Grams precipitate yielded.	f. Calculated yield of precipitated Ag_3PO_4 from grams $AgNO_3$ in columns c and d.	g. Calculated yield from grams Na_2HPO_4 in column b.	h. Grams Na_2HPO_4 not acted on by $AgNO_3$.	i. Percentage of silver in precipitated phosphate.
(1) Acid	0.7105	1.17872	....	0.9608	0.9700	2.09	0.4 (=57%)	76.96
(2) Neutralized by dilute KHO	0.7105	1.17872	....	0.9655	0.9700	2.09	0.4 (=57%)	75.82
(3) Acid	0.7105	.....	1.696 (excess)	1.0630	1.734	....	.....	76.19
(4) Neutralized by dilute KHO	0.7105	.....	1.696 (excess)	1.4070	1.734	....	.....	76.80
(5) Acid	0.7105	.....	2.544 (large excess)	1.1350	2.601	....	.....	76.65
(6) Neutralized as No. 4	0.7105	.....	2.544 (large excess)	2.3841	2.601	....	.....	77.36

case of the neutralized solution makes it evident that even in such menstrua the phosphate enters appreciably into solution.

It will be seen from (1) and (2), which are typical of a large number of determinations, that the "end-point" occurs at a stage in the reaction where only a partial separation of the phosporic acid as the silver salt has taken place. The resulting solution is acid to litmus, which acidity is due to the dihydrogen sodium orthophosphate; no free nitric acid could in any case be detected at this stage. It is evident, however, from these determinations and from Nos. 3, 4, 5 and 6 that equation (2) only expresses accurately what takes place when silver nitate is added to disodium orthophosphate and the completion of the reaction taken as being indicated by the first formation of argentic chromate.

As from these results it was evident that there remained a considerable quantity of phosphoric acid in combination as (presumably) dihydrogen sodium orthophosphate, silver nitrate was added in excess to effect its complete precipitation, if possible, and the precipitates analyzed. The results are expressed in percentages of silver which was determined first of all gravimetrically, but later on Volhard's method was substituted on account of the close agreement of the gravimetric estimations. The only one of the percentages in column (*j*) which *accurately* corresponds to the substance Ag_3PO_4 is No. 6, the others showing a deficiency in their silver content of from 0.4 to 1.54 per cent. But in the earlier stages of this investigation in four cases precipitates were obtained which yielded, on analysis, respectively :

	Silver. Per cent
(1) "End-Point" reaction	73.76
(2) "End-point" overstepped	74.19
(3) Large excess of silver nitrate	73.88
(4) Deficiency of silver nitrate	73.62
Average	73.862

These precipitates evidently correspond exactly to the formula $Ag_5H(PO_4)_2$ which contains 73.86 per cent. of silver. The others in Table I, numbered (1) to (5), lie between somewhere Ag_3PO_4 with 77.32 per cent. and $Ag_5H(PO_4)_2$ with 73.86 per cent. of silver.

The following table contains the percentage of silver found in a number of precipitates obtained under similar conditions of temperature and concentration, but in different total quantities

of the reacting salts. We have found it so far impossible to produce at will the phosphate of any desired composition but hope that further investigation will enable us to accomplish this.

TABLE II.—SILVER CONTENT IN PERCENTAGES.

73 per cent. and below 74 per cent.	75 per cent. and below 76 per cent.	76 per cent. and below 77 per cent.	77 per cent. and above.
73.49	75.34	76.47	77.01
	75.23	76.17	
	75.95	76.77	
	75.01	76.47	
	75.78	76.25	
		76.70	
		76.43	
		76.52	
		76.35	
		76.82	
		76.57	
		76.96	
		76.25	
		76.23	

It will be seen from this that the most commonly occurring precipitates nearly approach that of the composition Ag_3PO_4 *but not quite.*

Having obtained the "end-point" with potassium chromate (the reaction expressed by

$$2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3),$$

and having filtered off the precipitate, an excess of silver nitrate was added, causing further precipitation of a phosphate containing 76.25 per cent. to 76.5 per cent. of silver. The filtrate from this further precipitate was found to contain free nitric acid and also responded to tests for phosphoric acid. Following the equation given above, it would seem that the dihydrogen sodium phosphate reacted further with the silver nitrate possibly in accordance with the following equations :

(3) $$NaH_2PO_4 + AgNO_3 = AgH_2PO_4 + NaNO_3,$$

(4) $$AgH_2PO_4 + AgNO_3 = Ag_2HPO_4 + HNO_3,$$

(5) $$Ag_2HPO_4 + AgNO_3 = Ag_3PO_4 + HNO_3.$$

Combining these equations there would be obtained the expression

(6) $$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3,$$

which does not account for the presence of phosphoric acid in

the filtrates; but if (4) and (5) are coupled, the precipitate will have the composition $Ag_5H(PO_4)_2$ which was obtained in the four cases previously quoted, the production of which can be expressed by the equation

(7) $2Na_2HPO_4 + 5AgNO_3 = \underbrace{Ag_5H(PO_4)_2}_{Ag_3PO_4.Ag_2HPO_4} + 4NaNO_3 + HNO_3.$

For an expression which would account for the presence in the filtrate from the complete (?) precipitation of the silver, of both nitric acid and of phosphoric acid the following is suggested :

(8) $4Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 4NaNO_3 + HNO_3 + H_3PO^4$

It would appear then that the reaction between silver nitrate and disodium orthophosphate takes place in several distinct stages, and that the formation of a phosphate containing about 76 per cent. of silver is the most constant resultant. Also that free nitric acid and phosphoric acid remain in the solution from which no further precipitate can be obtained on the addition of the nitrate. It is our intention to further investigate this matter specially as regards the quantitative composition of these filtrates with a view to determining whether or not the last six equations suggested (Nos. 3 to 8) adequately express the reaction.

THE CHEMICAL LABORATORIES,
THE UNIVERSITY OF TORONTO.

86. "The interaction of hydrogen sulphide and sulphur dioxide." By William Robert Lang and Charles Macdonald Carson.

When hydrogen sulphide is passed into an aqueous solution of sulphur dioxide for several periods of from two to three hours on successive days, a milky solution is obtained which is termed Wackenroder's solution (Wackenroder, "On Pentathionic Acid," *Arch. Pharm.*, 1846, **48**, 272, 140; Berzelius, *Jahresbericht*, 1847, **27**, 36). This has been investigated by Debus (*Trans.*, 1888, **53**, 278), who proved the pre-

sence therein of sulphur, and sulphuric, trithionic, tetrathionic, and pentathionic acids, and probably hexathionic acid. The salts of these acids were examined by Hertlein (*Zeit. physikal. Chem.*, 1896, **19**, 287), who described methods for their separation and their physical properties. The explanation given by Debus for the formation of the polythionic acids is that tetrathionic acid is a direct product of the reaction of hydrogen sulphide on sulphurous acid, and that the other acids are formed from it by various subsequent reactions.

In order to investigate this, the reaction was effected, not in solution, but in the presence of a very little moisture, without which the gases do not interact. A large flask was surrounded with snow, a little moisture blown in, and the two gases then passed in at about equal rates for from two to three hours. A heavy yellow deposit, formed in the body of the flask, but not in the neck, was probably due to condensation of water having taken place only on the colder portions of the glass. This yellow material resembled ordinary sulphur, was dry to the touch, and quite brittle. On treatment with cold water, a milky liquid was obtained and the substance became stringy; this product, when boiled with water, was rendered soft and elastic.

Deposits formed by the above methods at different times, on being heated to 100° for an hour, lost from 25—30 per cent. by weight, and on estimating the sulphur compounds contained in them (as sulphuric acid) the amount never exceeded 1 per cent. Weighed quantities of the yellow material were allowed to remain in both open and closed tubes for several days at temperatures below 0°, but no change was noticeable in any case. When heated at 100°, the same loss of weight was observed as before; the presence of hydrogen sulphide could in no case be detected. Since the residue, after heating, contained more than 99 per cent. of free sulphur, it may be concluded that the polythionic acids were present in extremely small amounts.

Several quantities of the yellow material were next placed in stoppered bottles at the temperature of the room. After one day, the sulphur had become pliable and elastic and was covered with an oily liquid having an acid reaction, while a strong odour of sulphur dioxide was perceptible on removing the stoppers. The amount of this liquid seemed to increase after the second day, and this was proved to be the case on estimating the sulphuric acid present in quantities which had stood for one and two days respectively, and which had afterwards been heated at 100°. This liquid was then obtained in larger quantities, and was found to have a sp. gr. usually above 1.35, and to correspond with what is commonly called pentathionic acid, and which Debus showed to be a mixture of polythionic acids. Around the neck of the bottles, while below 0°, colourless crystals had formed: these were in such small amounts that their composition was not

determined, although, on warming, they gave off sulphur dioxide and left a deposit of sulphur.

It would appear from the above experiments that the action of gaseous hydrogen sulphide on gaseous sulphur dioxide produces first sulphur and water according to the equation,

$$2H_2S + SO_2 = S_3 + 2H_2O,$$

with sulphur dioxide present in the sulphur in considerable quantities. The last two substances slowly interact at comparatively higher temperatures, giving rise to polythionic acids.

An attempt was made to investigate the action of anhydrous liquid hydrogen sulphide on liquid sulphur dioxide, but the drying of the gases was probably not thorough enough. About 5 c.c. of liquid hydrogen sulphide were collected in a thick-walled glass tube surrounded by a freezing mixture, dry sulphur dioxide passed in until the volume of the mixed liquids measured some 15 c.c., and the tube then sealed at the blowpipe. A slight yellow deposit was formed where the tube was sealed. After one day, a thin yellow film had formed at the upper part of the tube which gradually increased, and when the tube was opened after one week there was found in the bottom a solid lump of sulphur covered by a clear liquid. This liquid when allowed to evaporate, gave off sulphur dioxide and left a small quantity of water containing dissolved sulphur dioxide.

Methods for the detection and estimation of the different polythionic acids which will, it is hoped, enable the composition of the oily mixture of acids to be accurately determined are at present being investigated.

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THE DETERMINATION OF BORIC ACID, ALONE AND IN THE PRESENCE OF PHOSPHORIC ACID.

BY

RODGER J. MANNING AND WILLIAM R. LANG.

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THE DETERMINATION OF BORIC ACID, ALONE AND IN THE PRESENCE OF PHOSPHORIC ACID.

BY RODGER J. MANNING AND WILLIAM R. LANG.

In a recent paper in this Journal, by Dr. Milton F. Schaak (1) on methods of estimating boric acid, mention is made of the compound formed by this acid and methyl alcohol in mixtures thereof, its distillation and collection over a weighed quantity of calcium oxide by which the ester is decomposed and the boric acid becomes fixed and, after ignition, is calculated by increase of weight (2).

Berzelius' method, used and recommended by Thaddeeff (3), depends on the formation of potassium borofluoride from the distilled trimethyl borate: its accuracy is, however, found to be doubtful owing to the imperfect insolubility of the compound (4). Other methods, such as that of Partheil and Bose (5) and that of Mylius and Meusser (6), are pronounced "unsatisfactory," "complicated" and "tedious."

This paper deals primarily with the separation of boric acid as the trimethyl compound and its subsequent gravimetric estimation as the barium salt. The first series of experiments is connected with this, the second has reference to volumetric methods of estimating boric acid in the distillate, and the last deals with its direct titration in mixtures of other acids.

I.—In order to determine, first, if boric acid is completely expelled as the trimethyl salt by distillation, quantities of from 0·5 to 1·5 grms. of boric acid (7) were placed in a retort, 250 c.c. of methyl alcohol added and the mixture distilled at a temperature of from 66° to 67° C., when it was found that after distillation at this temperature for an hour the residue in the retort contained only a small proportion of boric acid and, after one and a-half hours, none could be detected.

The estimation of the boric acid, thus expelled as the trimethyl compound, with barium chloride solution was proceeded with. Known amounts of boric acid were dissolved in methyl alcohol (8), placed in a retort, and the

distillate allowed to mix with a concentrated aqueous solution of barium chloride. The trimethyl borate reacts with the water according to the equation—

$$B(OMe)_3 + 3H_2O = B(OH)_3 + 3MeOH.$$

The boric acid thus liberated reacts with the barium chloride to form barium borate and free hydrochloric acid in which the former dissolves. Caustic alkali was then added and the resulting precipitate of barium borate, $Ba(BO_2)_2$, washed with alcohol till free from all traces of chlorides, dried at 110° C. and weighed on a tared filter. The resulting weights of precipitate were in all cases too high and this was found to be due to the presence of barium hydroxide which was precipitated on concentrating the solution from filtration (9). The proceeding was then modified to obviate this, and the liberated hydrochloric acid in the reaction—

$$2B(OH)_3 + BaCl_2 = Ba(BO_2)_2 + 2HCl + 2H_2O$$

neutralised accurately by means of semi-normal sodium hydroxide with phenolphthalein as indicator. The use of this strong solution of sodium hydroxide—and also of barium chloride—was necessary to prevent the solution of part of the barium borate in water, in which it was found to be appreciably soluble. Weighing the precipitated barium salt gave results corresponding to 99·68 per cent. of the theoretical.

Being now fully satisfied with the accuracy of this method, determinations of the boric acid in pure borax were undertaken. Amounts of borax of about 1 grm. were weighed out, mixed carefully with from 20 to 30 c.c. of concentrated sulphuric acid and added to 350 c.c. of methylated spirit (8) contained in a retort. An excess of sulphuric acid was found to be necessary to prevent the reprecipitation of the salt by the alcohol. The mixture was then subjected to distillation at a temperature of from 65°—70° C. and it was found advisable to keep the bulk of the alcoholic solution approximately constant by leading into the retort from a distilling flask a further supply of spirit. About 30 minutes sufficed to carry over most of the boron compound, but results showed it to be necessary to continue the distillation much longer. A period of one and a half hours was therefore chosen as the best time for the operation. The determination of the boric acid was done as described previously, and a number of estimations showed that the borax could be estimated in this way with only a very small error.

Wt. of borax taken.	Wt. of $Ba(BO_2)_2$.	Percentage found.
0·9728 grm.	1·1262	99·0
0·9700 ,,	1·1270	99·4
0·9364 ,,	1·0900	99·6

The presence of any appreciable comparative amount of water in the retort is to be avoided, as the trimethyl borate would then be decomposed, yielding the alcohol and boric acid, which would not distil over; the result would then be too low.

This method was further applied to mixtures containing phosphates and sulphates in addition to borates with perfectly satisfactory results.

2. *Volumetric estimation with previous distillation.*—As boric acid can be titrated with standard sodium hydroxide in the presence of glycerine, and the end-points in the formation of sodium borate indicated by phenolphthalein, several determinations were tried after decomposing the borate in alcoholic solution with sulphuric acid. The apparatus used was the same as in the previous experiments: the distillate was collected in water, made up to a litre and aliquot portions taken for titration. To each portion thus taken it was found necessary to have about one-third of the bulk of the solution glycerine[10]. The results of the titration gave 99·75 per cent. of the boron compound, this error—0·25 per cent.—being considerably less than the literature on the subject would lead one to expect.

3. *Direct volumetric estimation in the presence of phosphates and sulphates.*—A mixture of a phosphate, a sulphate[11] and a borate were treated with decinormal sulphuric acid till acid to Methyl Orange, thus setting free phosphoric and boric acids. Decinormal sodium hydroxide was then run in until the solution was neutral to Methyl Orange, which was found only to indicate the end of the formation of the sodium dihydrogen phosphate; a still further amount of alkali had to be added before the solution began to react alkaline with phenolphthalein showing that the disodium compound had been formed [12]. The boric acid not being neutralised at once in aqueous solution by alkali, glycerine was then added, and the titration of the boric acid completed. The results are given below from which the accuracy of the method may be seen:—

Amounts of $Na_2B_4O_7, 10H_2O$.	Amount formed by titration as above.	Per cent.	Error.
0·2390 grm.	0·2385 grm.	99·82	0·18
0·2990 ,,	0·2985 ,,	99·85	0·15
0·3824 ,,	0·3823 ,,	99·95	0·05
	Average	99·88	0·126

An error avoided here by titrating the solution previously with the sodium hydroxide till neutral or faintly alkaline, is the quantity of alkali of necessity absorbed by the water before the first trace of alkalinity is apparent. Experiments showed this to be an appreciable

amount: in the case of 50 c.c. alcohol and 50 c.c. water, 0·0016 grm. potassium hydroxide was required.

The authors intend applying these methods to the determination of boric acid in food stuffs.

(1) 1905, 609.
(2) See Gooch. Ann. Chem. J., 9, 23—33, and Montemartini Gazz. chim. ital., 28, 344—348.
(3) This J., 1898, 953.
(4) See (2) and (3).
(5) Ber., 1901, 3611.
(6) Ber., 1904, 397, and this J,, 1904, 269.
(7) The composition of the boric acid employed—whether $B(OH)_3$, HBO_2 or $H_2B_4O_7$,—was determined by estimating the amount of B_2O_3 contained in it. A weighed amount of boric anhydride, formed by fusing the boric acid to a clear glass, was dissolved in water and titrated against potash with phenolphthalein as indicator. A weighed amount of boric acid was also titrated against the same potash. Hence the percentage of B_2O_3 in the acid used was found. In these titrations—and all subsequent ones in the second part of this paper—25 to 30 per cent. of glycerine was used, as it is found that the neutralisation of boric acid by alkali cannot be done with any degree of accuracy except in the presence of glycerine or other polyatomic alcohol. (R. T. Thomson, this J., 1893, 432.)
(8) Ordinary methylated spirits (free from mineral oil) were found to act equally well.
(9) Pure sodium hydroxide was used, prepared from metallic sodium.
(10) See note (7). Also J. Amer. Chem. Soc., 1898, 288. The determinations were done before the above papers were noticed.
(11) The sulphate might have been omitted, as it took no part in the subsequent reaction.
(12) A strong solution of disodium hydrogen orthophosphate is slightly alkaline to phenolphthalein. Comparative experiments were made with varying amounts of a saturated solution of this salt and equal quantities of water; phenolphthalein added to each and decinormal potassium hydroxide added to the water till the shades of pink were identical:—

Phosphate solution in c.c. made up to 50 c.c.	Alkali required for 50 c.c. of water.
0·00	0·02 c.c.
0·50	0·06 ,,
1·00	0·08 ,,
2·00	0·09 ,,
3·00	0·10 ,,
4·00	0·11 ,,
5·00	0·12 ,,
6·00	0·12 ,,
7·00	0·12 ,,
8·00	0·12 ,,

For most solutions of this salt, therefore, a deduction of 0·1 c.c. would be the maximum correction necessary.

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A GENERAL METHOD OF CALCULATION IN KINETICS: THE METHOD OF AREAS. A METHOD OF APPROXIMATE EFFECTIVE AVERAGES.

BY RALPH E. DE LURY

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PART I. THEORETICAL

Introduction

In recent investigations in Chemical Kinetics there occur differential relations of the type,

$$\frac{dx}{dt} = K(A - x)^l (B - x)^m (C - x)^n \qquad (1)$$

where l, m, n, are positive or negative, and generally, though not always, integral. The problem is, in any case, to discover

values of K, l, m, n that suit the particular reaction. The method of solving it, is to assume values of l, m, n, and then to examine whether for different values of t and the corresponding values of x the value of K is constant. But to do this we need the integral of the equation (1), and this integral can seldom be found in a form that lends itself to ready computation. In such cases methods of approximation have been employed. A short discussion of these methods will first be given, and this will be followed by an account of a method which, though implying in the end a mechanical quadrature, is on its theoretical side, rigorous. Further, the area as found by the planimeter or other means, represents a degree of accuracy quite as high as the experimental data warrant.

Methods that have been used

(I) *Integration by Partial Fractions*

In equation (1) assume l, m, n, to be positive integers; then,

$$K\int_0^t dt = \int_0^x \frac{dx}{(A-x)^l(B-x)^m(C-x)^n}. \qquad (2)$$

Therefore,

$$Kt = \int_0^x \left[\sum_{r=1}^{r=l} \frac{L_r}{(A-x)^r} + \sum_{r=1}^{r=m} \frac{M_r}{(B-x)^r} + \sum_{r=1}^{r=n} \frac{N_r}{(C-x)^r}\right] dx. \qquad (3)$$

The integration yields $l + m + n - 3$ terms of the type,

$$-\frac{L_r}{r-1} \cdot \frac{1}{(A-x)^{r-1}}$$

and 3 terms such as,

$$L_1 . \log_e (A-x),$$

where L_r, M_r, N_r are functions of A, B, C, which can be determined, and hence K can be calculated.

When certain of the exponents l, m, n are negative the integral is evaluated in a somewhat similar manner.

This method is the one commonly employed and it im-

plies that l, m, n are integers. The calculation is complicated when some or any of the positive exponents are at all large. For the case, $l = m = n = 1$, the values are easily found.[1]

(II) *Integration by Series*

Equation (2) may be written,

$$KA^lB^mC^n\int_0^t dt = \int_0^x \left(1-\frac{x}{A}\right)^{-l}\left(1-\frac{x}{B}\right)^{-m}\left(1-\frac{x}{c}\right)^{-n} dx \qquad (4)$$

$$= \int_0^x \left[1 + x\left(\frac{l}{A}+\frac{m}{B}+\frac{n}{C}\right) + x^2\left(\frac{l(l+1)}{2A^2}+\frac{lm}{AB}+..\right)+..\right]dx.$$

Therefore,

$$R = \frac{x}{t}\left[1+\frac{x}{2}\left(\frac{l}{A}+\frac{m}{B}+\frac{n}{C}\right)+\frac{x^2}{3}\left(\frac{l(l+1)}{2A^2}+\frac{lm}{AB}+..\right)+..\right] \qquad (5)$$

where $R = K A^l B^m C^n$, that is, the initial rate.

This series is only rapidly convergent when the ratios, $\frac{x}{A}, \frac{x}{B}, \frac{x}{C}$, are small, and the calculation becomes tedious for values of these ratios greater than about one-fourth.

This method was used in calculating the values of R in the measurements of the rate of oxidation of potassium iodide by chromic acid.[2] The values of R are very close approximations. In the case where x was greatest (12 percent of the least concentration, A), an error of only 1 percent was made by neglecting the fourth term of the series in (5). When the coefficients of x^2, x^3, etc. are determined for any set of initial concentrations, the calculation of R (or K) is then very easy; this is therefore a good method to employ if there are many measurements in a set of experiments of the same initial concentrations.

(III) *Integration by Exponentials*

This method was introduced by Profs. W. Lash Miller and T. R. Rosebrugh.[3]

[1] Fuhrmann: Zeit. phys. Chem., 4, 89 (1889).

[2] De Lury: Jour. Phys. Chem., 7, 239 (1903). Expts. 15, 16, 17, 25, 26, 27.

[3] Trans. Roy. Soc. Canada, Sec. 3, 73 (1903).

Equation (1) may be transformed into

$$K_1 t = \int_x^q e^{-z} z^{-l}\, dz + r/q^2 \int_x^q e^{-z} z^{2-l}\, dz - s/q^3 \int_x^q e^{-z} z^{3-l}\, dz, \text{ etc.,} \qquad (6)$$

where K_1, q, r, s, and z are expressible in terms of A, B, C, l, m, n, and x.

Numerical values of certain of these functions have been computed; and by means of these tables the values of K can be calculated. The method is adapted to cases in which one concentration is smaller than the others and holds for all real values of the exponents.

(IV) *Direct Use of the Differential Equation*

W. C. Bray has recently described a method for the calculation of K from the differential equation.[1]

If, for example, the rate proceed in accordance with the equation:

$$dx/dt = K(A - x)(B - x)^2 \qquad (7)$$

he calculates values of k, defined by

$$dx/dt = k(A - x)$$

from successive pairs of x and t; and from them obtains K by the relation

$$K = \frac{k_1}{(B - x_1)^2} = \frac{k_2}{(B - x_2)^2} \qquad (8)$$

from which K can be calculated.

This method is particularly good when A is small relatively to the other concentrations. When there are several concentrations of about the same magnitude, and when the exponents are high, or are not integral, or are variable, difficulties arise in the use of this method; however, it should be of service in the study of complex reactions such as that treated by Bray in the paper cited.

[1] Jour. Phys. Chem., 9, 573 (1905).

The above methods are somewhat limited in their application. The last three methods are approximate, but they will furnish for many cases approximations sufficiently close. The following method, general in its application, evades computations except those numerical reductions necessary for the construction of the curve, gives results as accurate as the results of the experiments sanction, and reveals readily the values of the exponents.

The Method of Areas[1]

(I) *General Case*

Suppose the reaction to take place according to the following equation,

$$\frac{dx}{dt} = K.F(x). \tag{9}$$

We have then,

$$\int_o^x dx = K \int_o^x F(x).dt$$

and therefore,

$$x = K \int_o^x F(x).dt. \tag{10}$$

If the curve $F(x)$, t be plotted as in Fig. 1, where PQR is the curve $F(x)$ t we have,

[1] This method suggested itself to the writer in April, 1905, while studying a case of complex oxidation: "The Rates of the Reactions in Solutions Containing Arsenious Acid, Potassium Iodide, Potassium Bichromate, and Sulphuric Acid," which is about to be published. While writing the present paper his attention was called to the article on *Mittlere Geschwindigkeit* by A. Fuhrmann (Zeit. phys. Chem., 4, 520 (1889); also, "Differential- und Integralrechnung" by the same author), who has given an excellent mathematical treatment of the subject of *average rate*. The writer knows of no instance where the ideas given in this paper have been applied in the study of Chemical Kinetics.

$$x = K\int_0^x F(x).dt$$

$$= K \times \text{area (OPQRT)}. \qquad (11)$$

By methods described below, the area (OPQRT) can be found accurately and hence the constant K can be calculated

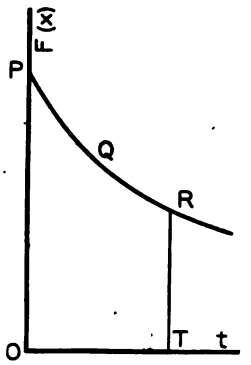

Fig. 1

for any assumed indices in the function, $F(x)$, and in this way the appropriate exponents can be determined.

Measurement of the Area

By using the experimental values of x, or preferably those taken from the x, t curve (as in Fig. 2), the function $F(x)$ can be calculated, and the curve $F(x)$, t (as in Fig. 1), can b plotted on section paper to a suitable scale (as large as possible). (*a*) The areas, $\int_0^x F(x).dt$, can then be quickly found by means of a planimeter. A good instrument will enable the operator to find the areas in question as accurately as the curve can be plotted (see Table VII, Part II). If a planimeter be not available the area may be calculated by employing certain approximate formul s for the area.

(*b*) By regarding the area as made up of a series of tra-

peziums of equal base, Δt, the area is expressed approximately thus,

$$\text{Area} = \Delta t(F_0 + F_1 + F_2 + \ldots\ldots + F_n) - \Delta t.\ \frac{F_0 + F_n}{2} \qquad (12)$$

where F_0, F_1, F_2, $\ldots\ldots F_n$, are the values of $F(x)$ when $t = 0$, Δt, $2\Delta t$, $\ldots n\Delta t$. This formula is easily applied and, in general, gives close approximations without taking n very large.

(*c*) Some of "Simpson's Rules"[1] may be applied, or the squares of the section paper may be counted, or if the paper is sufficiently heavy the areas may be found by weighing.

Reverse or Successive Reactions

Suppose we have,

$$\frac{dx}{dt} = K_1.F_1(x) \pm K_2.F_2(x) \qquad (13)$$

then,

$$x = K_1\int_0^x F_1(x).\,dt \pm K_2\int_0^x F_2(x).dt. \qquad (14)$$

This is the general relation showing the progress of a reaction. In many cases the amount of change due to reverse or successive reactions is negligible; sometimes also there are instantaneous successive reactions: in such cases equation (10) would be used in place of equation (14). When, however, the change due to reverse or successive reactions is not negligible, by plotting $F_1(x)$ and $F_2(x)$, the values of K_1 and K_2 can be found by means of equation (14), any two experimental values of x with their corresponding measured areas being used.

Equation (14) generally takes some such form as,

$$x = K_1\int_0^x (A - x)^l(B - x)^m.dt - K_2\int_0^x (C - x)^n(D - x)^r.dt. \qquad (15)$$

[1] See Williamson's Integral Calculus, p. 212.

It may be possible to determine one of the constants by choosing conditions such that the amount of change due to the other rate is negligible.[2] In many cases, however, this is not necessary, as equation (15) is easily applied.

(II) *Special Case*: $F(x) = A - x$

Let equation (10) take the form,

$$x = K\int_0^x (A - x).dt. \tag{16}$$

Then,

$$x = K(At - \int_0^x x.dt)$$

$$= K.\left\{\text{area (OPQT)} - \text{area (OSRT)}\right\}$$

$$= K.\text{ area (OPQRS)} \tag{17}$$

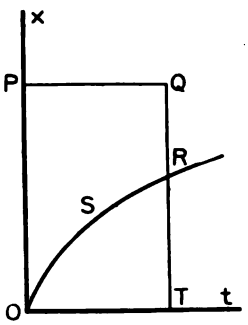

Fig. 2

where ORS is the curve x, t (Fig. 2), and OP = A.
Also,

$$\frac{x}{t} = K(A - \frac{1}{t}\int_0^x x.dt) \tag{18}$$

where $\frac{x}{t}$ is the *average rate* during the interval . = o to $t = t$,

[1] As in the case of iodide oxidation by arsenic acid: See Part II, Table I, for applications to this case.

and $\frac{1}{t}\int_0^x x.dt$ is the *effective average* value of $A - x$, that is, the effective average concentration of the chemical represented by A. Writing X for the effective average value of x that is, for $\frac{1}{t}\int_0^x x.dt$, we have,

$$\frac{x}{t} = K.(A - X). \tag{19}$$

(III) *Approximate Treatment: The Method of Approximate Effective Averages*

By extending the idea of effective averages a useful approximate formula is obtained as follows: If the reaction be represented by the equation,

$$\frac{dx}{dt} = K(A - x)(B - x)^m(C - x)^n \tag{20}$$

where B and C are large relatively to A, we have as a first approximation

$$\frac{x}{t} = K(A - X)\ (B - \tfrac{x}{2})^m\ (C - \tfrac{x}{2})^n \tag{21}$$

where X, as used above, has the value $\frac{1}{t}\int_0^x x.dt$. A much closer approximation is furnished by the following equation,

$$\frac{x}{t} = K(A - X)\ (B - X)^m\ (C - X)^n \tag{22}$$

where $A - X$, $B - X$ $C - X$, are *approximate effective average concentrations*. Under certain conditions equation (22) is a very close approximation (see Tables of Part II). The smaller the value of $m + n$ the closer the approximation; it is therefore very close when some of the exponents are negative. The difference between (22) and the exact equation (10) cannot be easily expressed mathematically.

(IV) *Application of the Above Methods to the Determination of the Exponents*

(*a*) Equation (22) may be employed in the form,

$$o = \log K + \log (A - X) + m.\log (B - X) + n.\log (C - X) - \log \frac{x}{t}. \quad (23)$$

By using a sufficient number of values of x and t, the numbers K, m, n, may be calculated approximately.

(*b*) For any assumed exponents, equation (10) can be easily tested. $F(x)$ is calculated by logarithms and if these be put down systematically it will be an easy matter to calculate this function for various sets of exponents. However, the following method may be employed:

Suppose,

$$dx = K.f_1(x).f_2(x) \quad (24)$$

where $f_1(x)$ and $f_2(x)$ are functions of x. If $f_2(x)$ be plotted and $f_1(x)$ be a simple function (such as $A - x$), we have as a close approximation,

$$x = f_1(X).\int_o^x f_2(x).dt. \quad (25)$$

For example, if,

$$x = K.\int_o^x (A - x)^l (B - x)^m (C - x)^n . dt$$

we have approximately,

$$x = K.(A - X)^r \int_o^x (A - x)^{l-r} (B - x)^m (C - x)^n . dt \quad (26)$$

where r is supposed small (*e.g.*, $r = 1$). So that if the function had been plotted for the exponents $l - r$, m, n the values of $K(A - x)^r$ and hence of K can be found very closely by means of equation (26). This approximation will be of use in tracing the change in r where r is variable, as in the case of iodide oxidized by chromic acid mentioned above).

PART II. PRACTICAL APPLICATIONS

In the following applications of the foregoing principles, the curves used in measuring the areas were plotted to a suitable scale on millimeter section paper. The areas were measured by means of a planimeter, the arm being adjusted so that a reading of 1000 corresponded to 100 square centimeters. No difficulty was experienced in getting duplicate readings to agree (see Table VII). These readings were then reduced to the proper unit.

(*I*) *Mr. Roebuck's measurements on the Rates of the Reactions in Solutions containing Arsenious, Arsenic, and Sulphuric Acids, Iodine and Iodide.*[1] (Table I).

(*A*) *Comparison of Different Methods of Calculation*

This case is chosen as it affords a ready means of comparing the results of several methods of calculation, namely, the exponential method (employed by Roebuck in his original paper), Bray's method of employing the differential equation, the method of areas, and the method of approximate effective averages.

When iodide is oxidized by arsenic acid, the arsenious acid and triiodide formed react reversely. According to Roebuck, the law governing the reaction (apart from a slight deviation in the exponents of the concentrations of iodide and sulphuric acid) is as follows,

$$\frac{dx}{dt} = K_1(C-x)(D-x)(E-x) - K_2x^2(C-x)^{-3}(D-x)^{-1}, \qquad (27)$$

where x denotes the amount of triiodide, and therefore the amount of arsenious acid formed, and C, D, E denote respectively the amounts of potassium iodide, sulphuric acid and arsenic acid initially present.

For this case then, equation (14) assumes the form:

$$x = K_1\int_0^x F_1(x).dt - K_2\int_0^x F_2(x).dt$$

[1] Roebuck: Jour. Phys. Chem., 6, 365 (1902); 9, 727 (1905). See also Bray: Ibid., 9, 573 (1905).

$$= K_1 \int_0^x (C-x)(D-x)(E-x)dt$$

$$- K_2 \cdot \int_0^x x^2 \cdot (C-x)^{-2} (D-x)^{-1} dt. \quad (28)$$

In Roebuck's notation, K_1 is $k_5 \cdot V^{-3}$, and K_2 is $k_3 \cdot V$, where V is the volume in litres.

(*a*) *Assuming* $K_2 \int_0^x F_2 \cdot dt = o$.

If we neglect the second term (representing the rate of oxidation of arsenious acid by triiodide) we may calculate k_5, which will then, of course, vary (in most of Roebuck's measurements this variation is negligible), by means of the equation,

$$x = k_5 \cdot V^{-3} \cdot \int_0^x (C-x)(D-x)(E-x)\,dt \quad (29)$$

or approximately (see equation (22)),

$$x = k_5 \cdot V^{-3} t\,(C-X)(D-X)(E-X) \quad (30)$$

where $X = \frac{1}{t} \int_0^x x.dt$, that is, the *effective average* value of x for the interval t.

The curves $F_1(x)$, t and x, t were plotted (as in Fig. 3), the areas, $\int_0^x F_1(x).dt$ and $\int_0^x x.dt$ measured, and the values of k_5 calculated employing equations (29) and (30). The constants thus calculated are denoted by (29),k_5 and (30),k_5 in the following table. In this table the values of t, x, and k_5 are taken directly from Roebuck's Table XXVIII. The values of (dif),k_5, that is, the constants calculated by using the differential equation (see equation (8)), are taken from Bray's Table XXVIII.

(*b*) *Assuming* $k_3 = 0.28$

The constant (31),k_5 is calculated from equation (28), assuming the value of k_3 to be 0.28 (as Bray does in calculat-

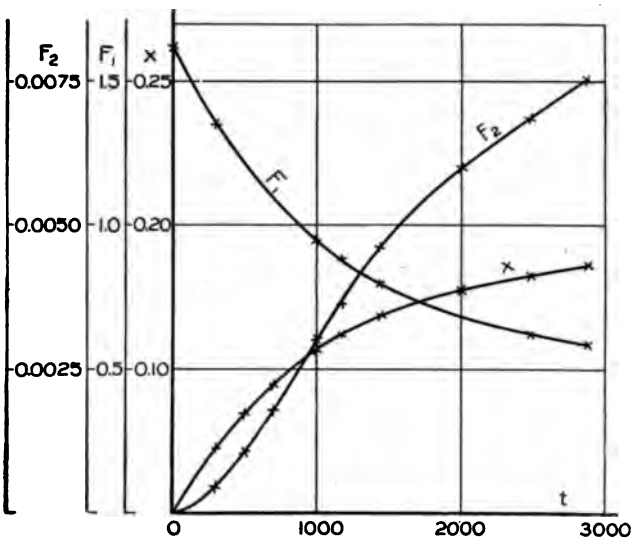

Fig. 3

ing (dif),k_5). For making this calculation the curve $F_2(x),t$ was plotted, and from the areas measured, (31),k_5 was obtained by means of the relation,

$$k_5 = (29),\ k_5.\ \frac{x + k_3.V.\int_0^x F_2(x).dt}{x} \qquad (31)$$

(*c*) *Comparison of the "Constants"*

It will be seen from Table XXVIII that (30),k_5 is practically identical with the "constant" (29),k_5, while k_5 which was calculated by the exponential method grows smaller and smaller as x increases, as would be expected. A comparison of (31),k_5 and (dif),k_5 shows the latter to be somewhat erratic. The reason that the various approximations are so close to those calculated by the area method, is that C and D are much larger (seven times) than E.

(*B*) *Calculation of* K_1 *and* K_2 *Assuming the Exponents as in Equation* (28)

K_1 and K_2 were calculated from equation (28), the two values of x necessary in each case being taken from successive measurements in Roebuck's Table XXVIII.

From these numbers the constants, (28),k_5 and (28),k_3 were calculated from the relations, $K_1 = (28), k_5.V^{-3}$ and $K_2 = (28),k_3.V$. The value of (28),k_5 is the same as the initial value of (29),k_5 in calculating which the other rate was neglected: this is natural, as of course the other rate is practically zero at the beginning of the experiment. The constant, (28),k_3, is found to be 0.049, that is, about one-sixth the value of k_3 (viz., 0.28) found in experiments where the concentrations were very different from those of Table XXVIII. This points to a change in the constant itself or (as Roebuck supposed) to a change in the values of the exponents, and shows that the *two* assumptions, viz., that $k_3 = 0.28$, and that the exponents are the same as in equation (28), cannot both be true for concentrations such as those used in the experiments of Roebuck's Table XXVIII. It is consequently not surprising to find that the constants (31),k_5 and (dif),k_5 rise in value—either the correction for the rate of oxidation of arsenious acid by triiodide is too great, or the exponents of the other rate are too low. It is also not surprising that $\frac{k_3}{k_5}$, calculated[1] on the above *two* assumptions, is five or six times greater than the equilibrium constant, K_6,[2] which is calculated on the one assumption. Since, moreover, the numbers, (28),k_3 and (28),k_5 (in the following Table I), are calculated on the *one* assumption that the exponents are the same as in equation (28), their quotient (the equilibrium constant) should be the same as K_6[2] of Roebuck's Table XXXIII, which was calculated on the same assumption,

[1] Roebuck: Loc. cit., p. 396, $\frac{k_3}{k_5} = \frac{0.28}{3.26 \times 10^{-7}} = 8.6 \times 10^5$, or better, $\frac{0.28}{3.7 \times 10^{-7}}$.

[2] Ibid: Table XXXIII, p. 395.

the concentrations being about the same in the two tables. Such we find to be the case, for,

$$\frac{(28),k_3}{(28),k_5} = \frac{0.049}{3.7 \times 10^{-7}} = 1.3 \times 10^5; \text{ and } K_e = 1\ 5 \times 10^5.$$

It is probable, however, that this value of the equilibrium constant is not correct, since the exponents of the equation (28) do not hold for the concentrations of the table from which it is calculated (see Roebuck s second paper).

(*C*) *Mr. Clark's Work on the Rate of Oxidation of Iodide by Bromate in Acid Solution*

Mr. R. H. Clark gives, in a paper about to be published, the following equation to represent the rate of oxidation of iodide by bromate in acid solution,

$$\frac{dx}{dt} = K(A - x)\ (B - x)\ (C - x)^2 \qquad (32)$$

where A, B, and C denote the amounts (in equivalents) of bromate, iodide and acid respectively, initially present, and x denotes the amount (in the same unit) of iodide oxidized in t minutes. Several investigators (see the above-mentioned paper) have studied this reaction, but have not interpreted their measurements as in (32). Some of their measurements have been recalculated, employing the approximate equation (see equation (22)),

$$x = Kt(A - X)\ (B - X)\ (C - X)^2 \qquad (33)$$

and also by using the exact relation,

$$x = K.\int_0^x F(x).dt$$

$$= K\int_0^x (A - x)\ (B - x)\ (C - x)^2.dt. \qquad (34)$$

Most of the measurements (as in Tables II–VI) could not be recalculated by any of the methods of approximation described in the preceding part, and since the reaction is of the fourth

TABLE I

C, 2.270; D, 2.293; E, 0.310; V, 0.155

t	x	$k_5.10^7$	$\frac{1}{t}\int_0^x x.dt$	(30), $k_5.10^7$	$F_1(x)$	$\int_0^x F_1(x).dt$	(29), $k_5.10^7$	$F_2(x)$	$\int_0^x F_2(x).dt$	(31), $k_5.10^7$	(dif), $k_5.10^7$	K_1	(28), $k_5.10^7$	K_2	(28), k_3
296	0.434	3.62	0.024	3.74	1.339	434	3.72	0.00040	0.035	3.84	4.0	—	—	—	—
994	0.113	3.22	0.064	3.50	0.926	1214	3.47	0.00303	1.15	5.00	5.6	0.000101	3.76	0.0073	0.047
1177	0.122	3.17	0.072	3.32	0.879	1378	3.30	0.00359	1.79	5.41	4.9	0.000105	3.91	0.0081	0.052
1432	0.137	3.07	0.084	3.26	0.795	1592	3.20	0.00460	2.83	6.14	6.5	0.000095	3.53	0.0078	0.050
2480	0.164	2.61	0.112	2.64	0.614	2316	2 64	0.00684	8.92	8.89	9.7	0.000099	3.68	0.0076	0.049
2880	0.171	2.34	0.120	2.49	0.579	2562	2.49	0.00752	11.82	9.98	9.8	0.000096	3.57	0.0072	0.047
											Avg.	0.00010	3.7	0.0076	0.049

K_1 was calculated, using equation (28); then K_2 was calculated, using the average value of K_1.

Equilibrium constant $K_6 = \frac{k_3}{k_5} = \frac{0.049}{3.7 \times 10^{-7}} = 1.3 \times 10^5$.

order the method of integrating by partial fractions would lead to rather involved computation.

In Tables II–VI are given recalculations of some of Magnanini's measurements (see Mr. Clark's paper for others). These tables are chosen as they afford a means of comparing the approximate equation (33) with the exact equation (34); the constants as calculated by these methods are denoted in the tables by (33), K and (34), K respectively. X is written for the effective average value of x, that is, for $\frac{1}{t}.\int_0^x x.dt$, and $F(x)$, as in (34), is written for $(A - x)(B - x)(C - x)^2$.

The fall in the constant (34),K in the earlier tables, as also the change in this "constant" from table to table, is possibly due to the fact that A, B, and C are the analytical and not the ionic concentrations.

TABLE II

A, 11.11; B, 7.41; C, 12.96; Vol. 10 cc.

t	x	$\int_0^x xat$	X	(33),K.10^7	10^{-3}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
5	0.83	2.40	0.48	144	99.8	58.3	142
12	1.44	10.8	0.90	124	77.6	121	119
13	1.46	12.4	0.95	119	75.9	126	116
21	1.84	25.2	1.20	113	63.9	183	100
25	2.05	32.0	1.28	100	57.9	207	99
41	2.73	70.0	1.71	98	41.3	283	93
52	2.97	101.6	1.96	94	38.3	326	91
84	3.69	209.2	2.49	94	23.7	419	88
91	3.81	236.0	2.59	95	22.1	431	89
175	4.82	608.0	3.47	102	10.8	560	86

TABLE III

A, 11.11; B, 7.41; C, 24.07; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K.10^7	10^{-2}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	0.82	0.88	0.44	99	477	82.5	99
3	1.05	1.68	0.56	88	367	120.5	87
9	2.35	12.40	1.38	86	339	279	84
15	3.27	29.04	1.94	89	209	384	85
17	3.38	35.52	2.09	87	141	412	81
28	4.38	78.4	2.80	90	133	519	84
31	4.50	91.7	2.96	90	77.3	540	83
35	4.68	110.3	3.15	90	73.7	557	84
40	5.10	134.6	3.36	95	66.0	593	86

TABLE IV

A, 11.11; B, 7.41; C, 35.18; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K.10^7	10^{-2}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	1.43	1.56	0.78	88	658	169	85
6	2.98	10.84	1.61	87	373	361	83
12	4.19	32.32	2.69	84	215	523	80
17	4.93	55.4	3.26	87	140	615	80
18	5.06	60.4	3.36	87	129	630	80
20	5.28	70.4	3.52	88	111	654	81

TABLE V

A, 11.11; B, 7.41; C, 46.29; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K.10^7	10^{-2}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	2.03	2.24	1.12	79	957	245	83
4	3.17	7.76	1.94	80	626	385	82
6	3.93	14.56	2.43	79	448	486	81
8	4.52	23.0	2.88	81	331	558	81
10	4.90	32.7	3.27	81	267	615	80
11	5.08	37.5	3.41	82	239	640	79

TABLE VI

A, 11.11; B, 7.41; C, 57.4; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33),K.10^7	10^{-3}.F(x)	$10^{-3}\int_0^x F(x).dt$	(34),K.10^7
2	2.55	2.92	1.46	70	1251	379	68
4	3.94	9.56	2.78	75	711	565	70
6	4.72	18.1	3.01	74	477	675	70
7	5.15	23.2	(3.71)	(79)	368	716	72
8	5.33	28.1	3.51	77	326	743	72

In all of the above tables, it will be seen that for small values of x, the "constant" (33),K and (34),K are practically equal. As x increases, however, the former gradually grows larger than the true "constant" (34),K, showing that the approximate value of x, namely,

$$Kt(A - X)(B - X)(C - X)^2, \qquad \text{(from equation (33))}$$

gradually falls off from the true value,

$$K\int_0^x (A - x)(B - x)(C - x)^2.dt, \qquad \text{(from equation (34))}$$

as x increases. The difference between these expressions becomes less and less as C is increased, until when C becomes four or five t mes the value of A, as in Tables IV and V, the two expressions become nearly equal; this is shown by the fact that (33) K and (34),K are nearly equal in these tables. Hence in general we have as a close approximation, if $\frac{x}{A}$ be not greater than $1/2$,

$$x = K.\int_0^x (A - x)^2 dt = Kt(A - X)^2. \qquad (35)$$

(D) Test of the Accuracy of the Method of Areas, and the Method of Approximate Effective Averages

The approximation (35) may be tested by assuming values of K,A,x, and the consequent values of t, and constructing

the two necessary curves: a suming K = 1, A = 10, and for x the values 1, 2, 3, 4, 5, 6, the values of (from the equation $t = \frac{1}{10 - x} - \frac{1}{10}$) become $\frac{1}{90}, \frac{2}{80}, \frac{3}{70}, \frac{4}{60}, \frac{5}{50}, \frac{6}{40}$, respectively. With these values of x and t, the curves x, t and $(A - x)^2, t$ were plotted and the two expressions for x in equation (35) were calculated from the measurements of the areas $\int_0^x x.dt$ and $\int_0^x (A - x)^2.d$ as made by the planimeter. Under the word "Reading" are given duplicate readings of the planimeter for the areas in question (Table VI), and X has its former meaning, namely, $\frac{1}{t}.\int_0^x x.dt$. The areas are expressed in the proper unit.

TABLE VII

t	x	Reading	$\int_0^x x dt$	X	$t(10 - X)^2$	Reading	$\int_0^x (10 - x)^2 dt$
0.0111	1.00	23; 23	0.00575	0.518	1.00	397; 396	0.99
0.0250	2.00	104; 103	0.0260	1.04	2.01	801; 802	2.00
0.0428	3.00	284; 283	0.0707	1.65	2.98	1198; 1199	3.00
0.0667	4.00	624; 626	0.156	2.34	3.91	1605; 1606	4.01
0.1000	5.00	1224; 1226	0.306	3.06	4.82	2005; 2005	5.01
0.1500	6.00	2332; 2330	0.583	3.89	5.60	2404; 2401	6.00

A comparison of the duplicate readings shows how closely areas can be measured by means of the planimeter: it is evident that these measurements can be made far more closely than a chemical analysis is usually made. Since x and $\int_0^x (10 - x)^2.dt$ are identical, the exactness of the method of areas can not be doubted. The value of the approximation,

$t(10 - X)^2$, differs from x by less than 4 percent when x is 5. It is evident from this, that equation (19) is applicable to the first half of bi-molecular reactions (and consequently to reactions of a higher order when all the concentrations but two, linearly involved, are practically non-variant). Hence in such cases equations (20) and (23) may be employed to calculate the values of the constant and the exponents, and where a deviation occurs in an exponent, to trace this variation. If desirable, a correction can be made by estimating the percentage error.

The above examples are sufficient to show the applicability of the Method of Areas and the Method of Approximate Effective Averages. At present I am employing these methods in the study of some cases of complex oxidation, and also in the recalculation of some kinetic measurements which have appeared in the chemical journals.

Summary

I. An outline of the methods that have been used in the computations occurring in the study of Chemical Kinetics, is given.

II. A "*Method of Areas*" is described. The Kinetic Equation is used in the following form,

$$x = K.\int_0^x F(x).dt$$

and in the case of reverse or successive reactions, in the form,

$$x = K_1.\int_0^x F_1(x).dt \pm K_2.\int_0^x F_2(x).dt.$$

The curve $F(x)$, t is plotted, the areas $\int_0^x F(x).dt$ are then measured by means of a planimeter, and the values of K are calculated from the values of x, and thus the correctness of

the assumed function, $F(x)$, is tested. The areas can be measured as accurately as the experimental data will warrant.

III. A "*Method of Approximate Effective Averages*" is described. The Kinetic Equation is used in the form,

$$\frac{x}{t} = K\left(A - \frac{1}{t}\int_0^x x.dt\right)^l \left(B - \frac{1}{t}\int_0^x x.dt\right)^m,$$

which is a close approximation under certain conditions. This equation may be used in the following form to calculate approximately the values of K, l, m,.. by taking a sufficient number of values of x,

$$o = \log K - l.\log\left(A - \frac{1}{t}\int_0^x x.dt\right) - m.\log\left(B - \frac{1}{t}\int_0^x x.dt\right) - .. - \log\frac{x}{t}.$$

The following equation may be used in some cases in tracing the variation in an exponent (r varying),

$$x = K\left(A - \frac{1}{t}\int_0^x x dt\right)^r \int_0^x (A - x)^{l-r} (B - x)^m .. dt.$$

IV. Some examples showing the applicability and accuracy of the above methods are given.

I am glad of this opportunity of expressing my gratitude to Professor W. Lash Miller. Without the training and help I have received from him, the above problems would doubtless never have occurred to me.

University of Toronto,
March, 1906

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No. 58: THE RATES OF THE REACTIONS IN SOLUTIONS CONTAINING POTASSIUM BROMATE, POTASSIUM IODIDE, AND HYDROCHLORIC ACID, BY ROBERT H. CLARK

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THE RATES OF THE REACTIONS IN SOLUTIONS CONTAINING POTASSIUM BROMATE, POTASSIUM IODIDE AND HYDROCHLORIC ACID

BY ROBERT H. CLARK

Among the earliest contributions to the literature of this subject is a paper by W. Ostwald,[1] who studied the reaction between hydrogen iodide and bromate in order to determine the accelerating influence of different acids. The author did not attempt to formulate a satisfactory kinetic equation, but calculated the velocity constant from the bi-molecular formula, and came to the conclusion that, in general, the accelerating influence of the different acids is proportional to their affinity constants,[2] the chief exception being in the case of chromic acid. I have carried out a number of experiments on the action of chromic acid, which will appear in a second communication.

In the same year W. Meyerhoffer[3] and O. Burchard,[4] working independently of each other, investigated the reaction, and both came to the conclusion that the rate could not be represented by the formula of the second order or by any other simple formula. Meyerhoffer ascribed the complications to the influence of the iodine formed by the reaction and proposed the equation $\frac{dx}{dt}=\frac{c\,(a-x)^2}{x}$, but it was shown later by Meyer[5] that this equation is not in agreement with the experiments.

In 1890 Gaetano Magnanini[6] made a great many measurements on the rate of this reaction; he, like Ostwald, studied the influence of different acids and noted that the acceleration caused by hydrochloric, nitric and sulphuric acids is not

[1] Zeit. phys. Chem., 2, 127 (1888).

[2] See however, Zeit. phys. Chem., 19, 599 (1891) and Table IV of the present paper, p. 684.

[3] Ibid., 2, 585 (1888).

[4] Ibid., 2, 796 (1888).

[5] Zeit. phys. Chem., 2, 830 (1888).

[6] Gazz. chim. Ital., 20, 377 (1890).

proportional to their concentrations, but failed to draw any general conclusions.

The next paper on the subject, A. A. Noyes'[1] "Contribution to the Knowledge of the Order of Polymolecular Reactions," contains four series of experiments by W. O. Scott, in which the initial concentrations of potassium bromate and iodide were varied, while in all the acid was present in constant excess. Comparison of the constants of the second and third order in the different series led to the conclusion that "the reaction between hydriodic and bromic acids is of the second order."

In the following year in a paper "On the Catalytic Effect of Hydrion on Polymolecular Reactions"[2] Noyes showed from certain of Magnanini's measurements, that the rate of the reaction between hydrobromic and bromic acids is proportional to the square of the concentration of the hydrion.

In spite of this large amount of work, however, the author of the most recent text-book on chemical kinetics[3] is of the opinion that "the course of the oxidation of hydriodic acid by the oxyacids of the halogens appears to be so intricate that a satisfactory application of the mass law has not yet been made." The measurements of the present paper show definitely the influence of the concentration of each reagent on the rate, and the extent to which the results are affected by the presence of the products of oxidation, *viz.*, iodine and bromide.

Plan of the Experiments

In these measurements, in order to trace the effect of the concentrations of each one of the chemicals separately, I have adopted a plan described by Mr. W. C. Bray[4] under the title "Method of Constant Rates" which consists in choosing the concentrations so that "while the amount of change accomplished in a suitable interval of time is sufficient for the

[1] Zeit. phys. Chem., 18, 118 (1890).

[2] Ibid., 19, 599 (1891).

[3] J. W. Mellor: "Chemical Statics and Dynamics," p. 103 (1904).

[4] Jour. Phys. Chem., 7, 93 (1903).

requirements of an accurate analysis, yet the fractional alteration in the concentrations of the reagents involved is so small that the rate may be treated as practically constant during the interval." Where the reaction has proceeded so far that this assumption could not be made, a correction has been applied for the small changes in concentrations of the reagents involved. In all cases these corrections are comparatively small, the conclusions to be drawn from the experiments being, in general, obvious enough, even without the correction.

Method of Working

Temperature.—All the measurements were made at 30°, this temperature being maintained by a thermostat within one-tenth of a degree.

Calibration.—All the pipettes used were calibrated by weighing the distilled water discharged, thirty seconds being allowed for drainage. The burettes were calibrated as described in "Ostwald's Hand- und Hilfsbuch," p. 103.

Details of an Experiment.—Each measurement contained in the following tables involved the preparation of a new reacting mixture. Portions of the stock solutions used in the measurements were kept in the thermostat in glass-stoppered flasks. The potassium bromate was added to a suitable volume of water in a wide-mouthed half-liter glass-stoppered bottle, while the potassium iodide and hydrochloric acid were pipetted into a large test-tube together with enough water to make up a volume of 80 cc. After pipetting out the solutions they were allowed to stand in the thermostat for five minutes, and then the contents of the test-tube were quickly poured into the bottle and shaken, the exact time of mixing being noted. The total volume of the reacting mixture was always 250 cc. When it was desired to stop the reaction the contents of the bottle were rapidly stirred, 10 cc of a half-saturated ammonium bicarbonate solution were thrown in, and the time was noted. The iodine liberated was then determined with hundredth-normal arsenite.

Stock Solutions

Potassium Bromate.—0.0206 F.[1] made from Merck's potassium bromate and standardized by decomposing a known volume with excess of potassium iodide and hydrochloric acid, adding excess of the solution of ammonium bicarbonate, and titrating against the volumetric sodium arsenite.

Potassium Iodide.—0.9890 F. neutralized (to litmus) by hydriodic acid and standardized gravimetrically with silver.

Potassium Bromide.—2.002 F. neutralized and standardized with silver.

Hydrochloric Acid.—Two solutions 0.9539 F. and 0.9542 F. respectively, by comparison (phenolphthaleïn) with a freshly prepared volumetric potash solution, which in turn was standardized with potassium bichromate.

Sodium Arsenite.—0.02504 F. As_2O_3 (0.10017 normal) prepared according to Mohr[2] and standardized with dry freshly sublimed iodine.

Iodine.—Approximately decinormal, prepared from freshly sublimed iodine and compared frequently with the sodium arsenite, the accurate titre so found being used in the calculations.

Ammonium Bicarbonate.—A half-saturated solution was kept under carbon dioxide; it was tested from time to time, and not used unless a distinct blue color was obtained by adding one drop of centinormal iodine to a mixture of 250 cc water, 10 cc ammonium bicarbonate, 10 cc potassium iodide and 3 cc starch.

The Starch was prepared fresh daily: 1 gram to the liter.

All these solutions were diluted to one-tenth their concentration to form the "stock solutions" and volumetric solutions referred to in the preceding section.

Explanation of the Tables

The numbers at the head of each table, divided by 100,000, give the gram-formula weights of each reagent initially present

[1] Formula weights per liter.

[2] Chemisch-Anal. Titrirmethode, 9th ed., p. 392.

in the 250 cc of reacting mixture. Under t is given the duration of the oxidation in minutes; under x the iodine liberated, expressed as cubic centimeters of 0.010017 normal arsenite solution; and under x' these values corrected for the falling off in concentration of the reagents.[1] $R_0 = \frac{dx}{dt}\ (x=o)$ is the "initial rate," *i. e.*, the number of cubic centimeters of hundredth-normal iodine liberated per minute in the 250 cc of reacting mixture whose composition is, and remains, that given at the head of the table. Under K is given the "constant of the fourth order" multiplied by 10^{13}.

The experiments of Table I are the standard with which are compared those of Tables II, III and IV where the concentrations of the bromate, iodide and acid respectively are doubled.

Effect of Bromate, Iodide and Acid

TABLE I

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15

t	x	x'	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.23	0.231	462	99
10	0.45	0.454	454	97
20	0.89	0.907	453	100
30	1.40	1.44	480	103
45	2.15	2.25	500	104
60	2.80	2.99	498	103
90	4.15	4.56	506	104

Average value, $R_0 = 481 \times 10^{-4}$

TABLE II

$KBrO_3$, 41; KI, 98.67; HCl, 95.15

t	x	x'	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.46	0.464	928	99
10	0.90	0.907	907	97
20	1.80	1.87	935	100
30	2.75	2.90	966	103
45	4.00	4.32	960	104
60	5.24	5 79	965	103
90	7.60	8.77	973	104

Average value, $R_0 = 948 \times 10^{-4}$

[1] See pages 681 and 685.

TABLE III

$KBrO_3$, 20.5; KI, 197.3; HCl, 95.15

t	x	x'	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.45	0.454	908	97
10	0.90	0.915	915	98
20	1.80	1.86	930	99
30	2.75	2.88	960	102
45	3.99	4.30	955	102
60	5.22	5.73	955	102
90	7.53	8.66	962	102

Average value, $R_0 = 936 \times 10^{-4}$

TABLE IV

$KBrO_3$, 20.5; KI, 98.67; HCl, 190.3

t	x	x'	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.92	0.934	1860	100
10	1.85	1.91	1910	102
20	3.62	3.74	1870	100
30	5.39	5.91	1970	105
45	7.75	8.87	1970	105
60	9.76	11.60	1930	102
90	13.93	18.01	2000	106

Average value, $R_0 = 1930 \times 10^{-4}$

Effect of Chlorion and of Atmospheric Oxygen on the Rate

In order to assure myself that the effect of the hydrochloric acid was due entirely to the concentration of the hydrion I made some measurements in which the concentration of the chlorion was doubled by adding sodium chloride. The rate was the same as in the absence of the salt. The addition of very large quantities of potassium chloride, however, retards the oxidation, see Tables IX and X and p. 688.

To find whether the results were affected by access of air,[1] I made some preliminary measurements in duplicate, one of each pair under ordinary conditions, and the other in an atmosphere of carefully purified carbon dioxide.[2] I

[1] Compare Zeit. phys. Chem., 2, 103 (1888), and Gazz. chim. Ital., 20, 382 (1890).

[2] See Dushman: Jour. Phys. Chem., 8 (1904).

failed to detect any difference in the rates in the two cases, and the subsequent measurements were carried out in air.

Effect of the Concentrations of Bromate, Iodide and Acid on the Rate

By comparing Table I with II, III and IV respectively it is readily seen that the velocity of the reaction is proportional to the first power of the concentrations of the bromate and iodide and to the second power of that of the acid, as represented by the equation:

$$\frac{1}{V}\cdot\frac{dx}{dt} = \frac{(A-x)}{V}\,\frac{(B-x)}{V}\,\frac{(C-x)^2}{V^2} \qquad (1)$$

This conclusion is confirmed by the constancy of K in the tables as calculated from the integrated form of the above equation:—

$$\frac{KABC^2t}{V^3} = x' = x + \frac{1}{2}\left(\frac{1}{A}+\frac{1}{B}+\frac{2}{C}\right)x^2 + \frac{1}{3}\left(\frac{1}{A}+\frac{1}{B}+\frac{3}{C}+\frac{1}{AB}+\frac{2}{AC}+\frac{2}{BC}\right)x^3 \qquad (2)$$

In the tables I have used the symbol x' for the quotient $KABC^2t/V^3$, because it gives the amount of iodine that would be liberated in t minutes if the solution retained its original composition throughout the experiment. The amount of iodine actually liberated, x, is naturally less than x', because of the decrease in concentration of the reagents as the reaction proceeds.

In calculating K the values of A, B and C denoting respectively the initial quantities of $KBrO_3$, KI and HCl have been expressed in the same units as x (see p. 683); thus $A = 6KBrO_3$, $B = 2/3KI$, $C = HCl$, according to the equation:

$$KBrO_3 + 9KI + 6HCl = 3KI_3 + KBr + 6KCl + 3H_2O.$$

For instance in the experiments of Table I, $A = 123$, $B = 65.78$, $C = 95.15$.

In each table the constant increases slightly as the reaction proceeds; no importance can be attached to this fact, however, as a change of from 0.05 to 0.1 cc of the hundredth-normal arsenite used in the analysis would account for the increase.

Effect of Bromide

Judson and Walker[1] have shown that potassium bromide, which is one of the products of the reaction between bromic acid and hydriodic acid, is itself oxidized by bromic acid; this reaction, however, takes place much more slowly than the oxidation of potassium iodide even when equivalent quantities are employed, and in the experiments of Tables I to IV the concentration of the bromide never reached 3 percent of that of the iodide. A few experiments in which small quantities of potassium bromide were added to the reacting mixture gave results identical with those in which no such addition had been made, so that it was not necessary to make any correction for the presence of this product of the reaction.

In this connection a number of experiments were undertaken to see whether the two reactions, *viz.*, the oxidation of potassium iodide and that of potassium bromide by bromic acid, take place independently in the solution. In Tables V and VII potassium bromide alone was present; in those of VI and VIII both bromide and iodide, the latter, however, in comparatively small quantity, as under like conditions the iodide is oxidized 58 times as rapidly as the bromide.

In the fourth column of Tables VI and VIII are entered the sums of the values of x' from Tables I and V, and IV and VII respectively; that is to say, the combined amounts of iodine which would have been liberated in solutions containing the bromide and iodide separately; in each case these sums are greater than the amount of iodine set free in the mixture, as given in column four of Tables VI and VII.

TABLE V

$KBrO_3$, 20.5; KBr, 2000; HCl, 95.15

t	x	x'
20	0.61	0.62
30	0.94	0.95
45	1.42	1.44
60	1.85	1.89
90	2.75	2.86

[1] Jour. Chem. Soc., 73, 411 (1898).

TABLE VI

$KBrO_3$, 20.5; KBr, 2000; KI, 98.67; HCl, 95.15

t	x	x' (mixture)	x' (Sum I and V)
20	1.28	1.31	1.52
30	1.87	1.93	2.39
45	2.75	2.87	3.67
60	3.40	3.58	4.84
90	5.31	5.80	7.82

[Note: As the concentrations of the reagents have the same effect on the rate of oxidation of bromide[1] as on that of iodide, the values of x' in Tables V and VII were calculated from equation (2).

In calculating x' (mixture) for Tables VI and VIII the concentration of the bromide has been regarded as constant, and x' has been computed by means of a modified form of equation (2), *viz.*:

$$x'=x+(1/2A+1/C)x^2+(x-y)^2/2B \qquad (2\ bis)$$

where y is the value of x in Table V, and $x-y$ is substituted for x in the term $x^2/2B$, y being regarded as the iodine liberated (in experiments VI) by the bromine set free by the action of bromate on bromide, and $x-y$ that liberated by direct action of bromate on iodide.]

TABLE VII

$KBrO_3$, 20.5; KBr, 2000; HCl, 190.3

t	x	x'
20	2.40	2.46
30	3.76	3.91
45	5.39	5.70
60	7.00	7.50
90	9.71	10.71

[1] Judson and Walker: loc. cit.

TABLE VIII

$KBrO_3$, 20.5; KBr, 2000; KI, 98.67; HCl, 190.3

t	x	x' (mixture)	x' (Sum IV and VII)
20	4.75	5.01	6.20
30	7.35	7.98	9.82
45	10.60	12.02	14.57
60	13.40	15.73	19.10
90	18.58	23.43	28.72

The difference between "x' mixture" and "x' sum" in Tables VI and VIII was found to be due to the presence of the large quantities of potassium salts, which, as the readings of Tables IX and X show, retard the oxidation of potassium iodide.

The solutions used in the experiments of these two Tables (IX and X) are the same as those of Tables I and IV, with the addition of enough potassium chloride to make the concentration of the potassium ion the same as in the experiments of Tables V and VII. As is shown in the last columns of Tables IX and X, the iodine liberated in solutions containing both iodide and bromide is the sum of that liberated in solutions containing iodide alone, *plus* the iodine equivalent of the bromide liberated in the absence of iodide. Thus, the two reactions—oxidation of iodide by bromic acid, and oxidation of bromide by bromic acid—proceed independently in the same solution.

TABLE IX

$KBrO_3$, 20.5; KCl, 2000; KI, 98.67; HCl, 95.15

t	x	x'	x' (Sum V and IX)	x' mixture (VI)
20	0.67	0.68	1.30	1.31
30	1.01	1.03	1.97	1.93
45	1.49	1.54	2.96	2.87
60	1.85	1.93	3.78	3.58
90	2.91	3.10	5.85	5.80

TABLE X

$KBrO_3$, 20.5; KCl, 2000; KI, 98.67; HCl, 190.3

t	x	x'	x' (Sum VII and X)	x' from VIII
20	2.65	2.76	5.22	5.01
30	4.00	4.28	8.19	7.98
45	5.85	6.48	12.18	12.02
60	7.39	8.31	15.81	15.73
90	10.79	13.06	23.77	23.43

This simple relation makes it very easy to allow for the effect of the bromide which is formed from the bromate by the action of hydriodic acid. Judson and Walker have shown that the form of the equation for the rate of oxidation of bromide by bromate is the same as that of my equation 1; and the value of its constant calculated from the experiments of Table V, corrected for the high concentration of the potassium ion, and expressed in my units, is 2.2×10^{-13}.

The bromine formed by the oxidation of the bromide would, of course, react instantaneously with the potassium iodide, and liberate an equivalent amount of iodine, so that the total amount of iodine liberated in the time t is governed by the following differential equation, in which D represents the number of equivalents of bromide initially present.

$$\frac{dx}{dt}=(A-x)(C-x)^2\left[100 \times 10^{-13}(B-x)+2.2 \times 10^{-13}(D+x)\right]V^{-3}. \quad (3)$$

In all the experiments of this paper, except those in which potassium bromide was added at the beginning, $D=0$, and the last term of equation (3) may be neglected.

Effect of Iodine

The only other product of the reaction which might influence the rate is iodine. In order to study its effect I undertook the experiments of Table XI in which iodine was dissolved in the stock solution of potassium iodide and its amount determined by titration.

The first column of the table gives the amount of free iodine initially present in the reacting mixture expressed in

cubic centimeters of 0.010017 normal arsenite; the second, under "KI Corr.," the potassium iodide initially present, which was calculated by subtracting one-half the number in the first column from 98.67 (which was the amount of potassium iodide in the solution before addition of iodine), according to the equation:

$$KI + I_2 = KI_3.$$

Under x is entered the amount of iodine liberated during the time t (minutes), obtained by subtracting the initial iodine from the "titration." Under "x calc" is given the amount of iodine that would be liberated in the same time in solutions which contained throughout the experiment the amount of bromate and acid entered at the head of the table, and the amount of potassium iodide entered in the second column under "KI corr.," but no "initial iodine."

It will be noted that the difference between "x" and "x calc." entered in the last column of Table XI, although small, are all positive, and increase with increase in the amount of iodine present. This is in accord with the results of Mr. Dushman's measurements on the rate of oxidation of potassium iodide by iodic acid in the presence of free iodine, and points to the oxidation of triiodion by bromic acid.

The correction for this subsidiary reaction is so small, however, that the relations between concentrations and rate given by equation 2 should hold whether free iodine be present or not, and the equation should be able to account for the whole progress of the reaction between bromic and hydriodic acids from its commencement to its end. This conclusion is borne out by the experiments recorded in Table XLI of the Appendix, for which I am indebted to Mr. F. C. Bowman, where the value of K remains constant within 1 or 2 percent while 95 percent of the bromate is reduced.

Temperature Coefficient

To find the temperature coefficient, I made a series of measurements at 30°, 25° and 0° C.

TABLE XI

$KBrO_3$, 20.5; KI, 98.67; HCl, 190

Initial I	KI corr.	*t*	Titration	*x*	*x* calc.	Diff.
0	98.67	60	9.60	9.60	9.52	0.08
0	98.67	90	13.40	13.40	13.31	0.09
0	98.67	120	16.75	16.75	16.66	0.09
7.73	94.80	60	17.07 17.06	9.33	9.15	0.18
7.73	94.80	90	20.68 20.75	12.98	12.80	0.18
7.73	94.80	120	23.88 23.90	16.16	15.99	0.17
11.75	92.80	60	20.75 20.78	9.01	8.94	0.07
11.75	92.80	90	24.70 24.58	12.89	12.56	0.33
11.75	92.80	120	27.78 27.78	16.03	15.75	0.28
16.78	90.28	60	25.77 —	8.99	8.74	0.24
16.78	90.28	90	29.59 —	12.81	12.32	0.49
16.78	90.28	120	32.43 32.50	15.70	15.38	0.32
20.92	88.21	60	29.88 29.82	8.93	8.60	0.33
20.92	88.21	90	33.51 33.46	12.56	12.07	0.49
20.92	88.21	120	36.60 36.42	15.59	15.16	0.43
40.54	78.40	60	48.26 —	7.72	7.60	0.12
40.54	78.40	90	51.46 51.43	10.91	10.74	0.17
40.54	78.40	120	54.70 54.58	14.10	13.51	0.59
52.40	72.47	60	60.05	7.65	7.13	0.52
52.40	72.47	90	63.09 62.94	10.62	10.02	0.60
52.40	72.47	120	65.98 65.86	13.52	12.66	0.86

TABLÆ XIII

$KBrO_3$. 20.5; KI, 98.67; HCl, 190.3

	At 30°				At 25°					At 0°				
t	*x*	*x'*	R	K.10^{13}	*x*	*x'*	R	K.10^{13}	Coeff.	*x*	*x'*	R	K.10^{13}	Coeff.
20	3.46	3.67	183	98	2.58	2.70	135	72	1.84	0.65	0.66	33	17	—
30	5.10	5.57	185	99	3.81	4.07	136	72	1.85	0.88	0.89	30	16	1.84
45	7.50	8.55	190	101	5.65	6.23	138	74	1.89	1.30	1.33	29	16	1.87
60	9.60	11.39	189	100	7.29	8.28	138	74	1.87	1.75	1.80	30	16	1.85
90	13.40	17.23	191	102	10.37	12.48	139	74	1.89	2.58	2.70	30	16	1.85
120	16.75	23.45	195	104	13.13	16.75	139	74	1.97	3.38	3 58	30	16	1.87

The average value of the "temperature coefficient" of the rate, or the factor by which the rate is multiplied for a rise of 10° in the temperature, may be found by taking the cube root of the ratio between the rates at 30° and 0° C.; it is 1.85. The coefficients determined from the measurements at 30° and 25° C. (which are entered in the table "at 25°") are practically the same, or if anything, a little higher, see Table XIII.

Appendix

Magnanini's experiments, carried out in 1890,[1] some of those of Ostwald's[2] and the experiments of Noyes[3] are here recalculated.

At the head of each table I have given the initial composition of the reacting mixture, the numbers divided by 100,000 denoting gram-formula weights of the reagent initially present, the volume being 10 cc in all of Magnanini's and Ostwald's measurements, while in Noyes' the numbers recorded are for a volume of 1 litre. In all these experiments the temperature was 25° C. Mr. F. C. Bowman's experiments were carried out in this laboratory at 0° C., and the numbers recorded from his experiments are for a volume of 1 litre.

[1] Gazz. chim. Ital., 20, 377 (1890).

[2] Zeit. phys. Chem., 2, 127 (1888).

[3] Ibid., 18, 118 (1890).

In the first column of the tables (under t) is entered the duration of the experiments in minutes; in the second, the amount of iodine liberated x (in cubic centimeters of $n/100$ thiosulphate); where Magnanini gave the result of duplicate experiments, I have taken the average. In the third and last column I have entered the value of the constant K of the equation:

$$\frac{1}{V}\cdot\frac{dx}{dt} = K(A-x)\,(B-x)\,(C-x)^2V^{-4}$$

where A, B and C are taken from the heads of the table, and V is the volume in litres, *e. g.*, for Table XV, A = 11.11, B = 7.41, C = 24.07, V = 0.01. See page 685.

In computing the values of K, I made use of "The Method of Areas," described by Mr. R. E. De Lury.[1]

In order to facilitate comparison of the values of K so obtained, I have brought them together in the last table. The constants bracketed have been calculated from the experimental data by making use of the temperature coefficient 1.85 obtained from Table XIII. In the experiments where excess of hydrochloric or nitric acid was used, Magnanini's values agree with my own for the same temperature; replacing these monobasic acids by sulphuric acid, takes about 33 percent of K, corresponding to a difference of 12 percent in the dissociation, which is a fair agreement with the results of measurements of the electrical conductivity. In the experiments in which the concentration of the hydrion was large, the constants are uniform; where however their concentration is small, the constant shows a falling off. This is in line with the results of Mr. W. C. Bray's experiments on the oxidation of hydrogen iodide by chloric acid.[2]

The values of the constants derived from Ostwald's measurements are somewhat smaller than those from the corresponding measurements of Magnanini. Addition of chloric acid and of hydrobromic acid increases the constant

[1] Jour. Phys. Chem., 10, 425 1906.

[2] Ibid., 7, 92 (1903).

very slightly, due no doubt to the oxidation of the bromion or to the reduction of the chlorate.

Noyes and Scott worked with the potassium salts of bromic acid and hydriodic acid in presence of a constant amount of hydrochloric acid; their constant agrees very closely with my own.

Magnanini's Measurements

TABLE XIV

$HBrO_3$, 1.85; HI, 11.11

t	x	$K \times 10^{13}$
5	0.82	142
12	1.44	119
13	1.46	116
21	1.84	100
25	2.05	99
41	2.72	93
52	2.96	91
84	3.69	88
91	3.80	89
175	4.82	86

TABLE XV

$HBrO_3$, 1.85; HI, 11.11; HCl, 11.11

t	x	$K \times 10^{13}$
2	0.82	99
3	1.05	87
9	2.35	84
15	3.27	85
17	3.38	81
28	4.38	84
31	4.50	83
35	4.68	84
40	5.10	86

TABLE XVI

$HBrO_3$, 1.85; HI, 11.11; HCl, 22.22

t	x	$K \times 10^{13}$
2	1.43	85
6	2.98	83
12	4.19	80
17	4.93	80
18	5.06	80
20	5.28	81

TABLE XVII

$HBrO_3$, 1.85; HI, 11.11; HCl, 33.33

t	x	$K \times 10^{13}$
2	2.03	83
4	3.17	82
6	3 93	81
8	4.52	81
10	4.90	80
11	5.08	79

TABLE XVIII

$HBrO_3$, 1.85; HI, 11.11; HCl, 44.44

t	x	$K \times 10^{13}$
2	2.55	68
4	3.94	70
6	4.72	70
7	5.15	72
8	5.33	72

TABLE XIX

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 22.22

t	x	$K \times 10^{13}$
2	1.37	82
6	2.88	78
12	4.19	77
17	4.84	77
19	5.14	78

TABLE XX

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 33.33

t	x	$K \times 10^{13}$
2	2.03	77
4	3.06	73
6	3.83	72
8	4.41	72
10	4.89	72
11	5.03	72

TABLE XXI

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 44.44

t	x	$K \times 10^{13}$
2	2.57	68
4	3.80	67
6	4.60	66
8	5.19	67

TABLE XXII

$HBrO_3$, 1.85; HI, 11.11; H_2SO_4, 5.55

t	x	$K \times 10^{13}$
2	0.68	81
9	2.10	71
17	3.07	69
31	4.20	69
46	4.81	67
51	4.94	66
56	5.27	68

TABLE XXIII

$HBrO_3$, 1.85; HI, 11.11; H_2SO_4, 11.11

t	x	$K \times 10^{13}$
2	1.04	57
9	2.99	53
20	4.51	52
25	4.87	52
28	5.11	52
31	5.26	52

TABLE XXIV

$HBrO_3$, 1.85; HI, 11.11; HCl, 22.22

t	x	$K \times 10^{13}$
2	1.83	43
9	4.32	39
12	4.95	39
13	5.09	39
17	5.55	38

TABLE XXV

$HBrO_3$, 5.55; HI, 11.11

t	x	$K \times 10^{13}$
2	1.23	106
6	2.55	96
9	3.25	95
12	3.78	94
15	4.23	93
21	4.88	93
23	5.02	95
24	5.02	91
27	5.34	92

TABLE XXVI

$HBrO_3$, 9.26; HI, 11.11

t	x	$K \times 10^{13}$
2	2.30	91
4	3.56	90
6	4.36	89
8	4.94	88
10	5.43	89

TABLE XXVII

$HBrO_3$, 1.85; $KBrO_3$, 3.70; HI, 11.11

t	x	$K \times 10^{13}$
2	0.83	116
6	1.85	107
9	2.46	107
12	2.75	99
17	3.41	99
20	3.60	96
28	4.25	96
41	4.86	95
46	5.15	96

TABLE XXVIII

$HBrO_3$, 1.85; $KBrO_3$, 9.25; HI, 11.11

t	x	$K \times 10^{13}$
2	1.38	104
6	2.68	88
9	3.36	88
12	3.87	87
18	4.65	87
22	4.97	87
25	5.16	86

Ostwald's Measurements

TABLE XXIX

$HBrO_3$, 1.856; HI, 11.11

t	x	$K \times 10^{13}$
1	0.22	—
21	1.89	93
41	2.81	92
81	3.93	94
146	4.83	94
201	5.37	96
301	5.89	96
431	6.36	98

TABLE XXX

$HBrO_3$, 1.856; HI, 11.11; H_2SO_4, 5.55

t	x	$K \times 10^{13}$
9	2.04	59
17	3.07	61
31	4.17	63
56	5.27	64
71	5.67	64
97	6.14	65
115	6.39	65

TABLE XXXI

$HBrO_3$, 1.85; HI, 11.11; HCl, 11.11

t	x	$K \times 10^{13}$
9	2.46	85
17	3.54	84
31	4.63	84
41	5.20	85
51	5.60	86
61	5.90	87
71	6.20	85

TABLE XXXII

$HBrO_3$, 1.85; HI, 11.11; HNO_3, 11.11

t	x	$K \times 10^{13}$
9	2.44	84
17	3.51	82
31	4.63	82
41	5.18	84
51	5.55	81
61	5.86	80
71	6.09	80

TABLE XXXIII

$HBrO_3$, 1.85; HI, 11.11; $HClO_3$, 11.11

t	x	$K \times 10^{13}$
9	2.54	90
17	3.54	88
25	4.35	89
33	4.77	88
41	5.18	88
51	5.56	88
61	5.85	89

TABLE XXXIV

$HBrO_3$, 1.85; HI, 11.11; $HClO_4$, 11.11

t	x	$K \times 10^{13}$
9	2.43	85
17	3.52	82
25	4.25	84
33	4.71	83
41	5.15	84
51	5.56	85
61	5.78	85

TABLE XXXV

$HBrO_3$, 1.85; HI, 11.11; H_2SO_3, 5.55

t	x	$K \times 10^{13}$
9	2.40	81
17	3.41	80
25	4.16	81
33	4.65	81
41	5.05	81
51	5.40	81
61	5.76	81

TABLE XXXVI

$HBrO_3$, 1.85; HI, 11.11; HBr, 11.11

t	x	$K \times 10^{13}$
9	2.59	89
17	3.68	90
25	4.43	92
33	4.94	93
41	5.34	94
51	5.72	95
61	6.04	96

Noyes' Measurements

TABLE XXXVII

$KBrO_3$, 166; KI, 1000; HCl, 4000

t	x	$K \times 10^{13}$
2	112	63
4	192	62
7	279	62
11	358	62
16	423	62
22	479	62
30	526	62
40	562	62

TABLE XXXVIII

$KBrO_3$, 83; KI, 500; HCl, 4000

t	x	$K \times 10^{13}$
1.5	46	65
3	88	68
5	125	66
8	180	70
12	233	70
17	261	72
23	294	73

TABLE XXXIX

$KBrO_3$, 83; KI, 1000; HCl, 4000

t	x	$K \times 10^{13}$
1.5	48	68
3	90	68
5	134	68
8	179	65
12	223	63
17	258	60
23	290	60

TABLE XL

$KBrO_3$, 83; KI, 500; HCl, 4000

t	x	$K \times 10^{13}$
2.5	40	68
5.5	79	68
9	112	72
15	155	71
23	194	72
36	235	74
58	275	71

F. C. Bowman's Measurements

TABLE XLI

$KBrO_3$, 55.26; KI, 4960; H_2SO_4, 1666.6

t	x	Percent bromate decomposed	$K \times 10^{14}$
6	62.4	18.8	98
19	155.8	46.8	98
30	206.6	62.3	99
40	238.8	72.1	99
50	261	78.7	98
60	276.4	83.3	97
70	290.2	87.6	97
80	299.6	90.2	97
100	315.6	95.1	98

TABLE XLII
SUMMARY OF TABLES

Experimenter	Table	Initial Composition (Vol. = one litre)	$K \times 10^{13}$ for 30° C	$K \times 10^{13}$ 25° C	$K \times 10^{13}$ 0° C
Clark:	XIII	$KBrO_3$, 82; KI, 394.7; HCl, 760	100	73	16
Magnanini:	XIV	$HBrO_3$, 185; HI, 1111	(139)	102	(22)
	XV	" " + HCl, 1111	(117)	86	(19)
	XVI	" " + HCl, 2222	(112)	82	(18)
	XVII	" " + HCl, 3333	(111)	81	(18)
	XVIII	" " + HCl, 4414	(96)	70	(15)
	XIX	" " + HNO_3, 2222	(107)	78	(17)
	XX	" " + HNO_3, 3333	(100)	73	(16)
	XXI	" " + HNO_3, 4444	(92)	67	(15)
	XXII	" " + H_2SO_4, 555	(96)	70	(15)
	XXIII	" " + H_2SO_4, 1111	(73)	53	(12)
	XXIV	" " + H_2SO_4, 2222	(55)	40	(9)
	XXV	$HBrO_3$, 555; " — —	(130)	95	21)
	XXVI	$HBrO_3$, 1111; " — —	(122)	89	(19)
	XXVII	$HBrO_3$, 185; HI, 1111 + $KBrO_3$, 370	(137)	100	(22)
	XXVIII	" " + $KBrO_3$ 925	(123)	90	(20)
Ostwald:	XXIX	$HBrO_3$, 185; HI, 1111	(130)	95	(21)
	XXX	" " + H_2SO_4 555	(86)	63	(14)
	XXXI	" " + HCl, 1111	(116)	85	(19)
	XXXII	" " + HNO_3, 1111	(112)	82	(18)
	XXXIII	" " + $HClO_3$, 1111	(120)	88	(19)
	XXXIV	" " + $HClO_4$, 1111	(115)	84	(18)
	XXXV	" " + H_2SO_3, 555	(111)	81	(18)
	XXXVI	" " + HBr, 1111	(127)	93	(20)
Noyes and Scott:	XXXVII	$KBrO_3$, 166; KI, 1000; HCl, 4000	(85)	62	(14)
	XXXVIII	" KI, 500; HCl, 4000	(94)	69	(15)
	XXXIX	$KBrO_3$, 83; KI, 1000; HCl, 4000	(89)	65	(15)
	XL	" KI, 500; HCl, 4000	(97)	71	(16)
Bowman:	XLI	$KBrO_3$, 55.26; KI, 4960; H_2SO_4 16.6	(71)	(45)	10

Summary

(1) The rate at which iodine is liberated in solutions containing potassium bromate, potassium iodide and hydrochloric acid is proportional to the concentration of the bromate, the concentration of the iodide, and the square of the concentration of the acid.

(2) In solutions containing potassium bromate, iodide, bromide and hydrochloric acid the two haloid salts are oxidized independently.

(3) The potassium triiodide formed by the oxidation of iodide adds very slightly to the rate of reduction of bromate; so that, in first approximation, the effect on the rate produced by the iodine liberated during the reaction may be neglected.

(4) Thus the progress of the reaction may be expressed by a simple differential equation (see equation 1, p. 685), which is shown to be in accordance with the experiments. A term to represent the effect due to the bromide formed during the reaction may be introduced into the equation (see equation 3).

(5) Raising the temperature 10° multiplies the rate by 1.85.

(6) The equations developed in this paper have been used to recalculate Magnanini's, Ostwald's and Noyes' measurements. (See Appendix.)

These measurements were carried out in the chemical laboratory of the University of Toronto during the winter of 1904–5; and in conclusion, I wish to express my sincerest thanks to Prof. W. Lash Miller for suggesting this research and for his supervision throughout the work.

The University of Toronto,
June, 1906

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STUDIES

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LABORATORIES

No. 59: ON THE MECHANISM OF INDUCED REACTIONS,
BY W. LASH MILLER

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. XI.)

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ON THE MECHANISM OF INDUCED REACTIONS

BY W. LASH MILLER

The word "Induction," in the sense in which it is used in this article, was introduced into the chemical vocabulary by F. Kessler, in 1863.

"Let Rα and Rβ be two reducing agents" (wrote Kessler[1]), Oα and Oβ two oxidizing agents, such that under certain conditions Rα reacts easily with Oα while Rβ and Oβ react with difficulty or not at all. If then, on bringing all four substances together under these conditions, we find that the reaction between Rβ and Oβ is accelerated, we will regard this reaction as "induced" by that taking place between Rα and Oα. In most cases, at least so far as my knowledge goes, this general case is specialized, either by Oα being identical with Oβ, or Rα with Rβ. To distinguish these two cases, I shall call the former "induced oxidation" and the latter "induced reduction."

A large number of experimental and theoretical papers dealing with the subject of chemical induction have appeared since Kessler's time; lists are given by Manchot,[2] Engler and Weissberg,[3] Schilow,[4] Luther,[5] and Mellor.[6]

The term "induced reaction" is now generally restricted to Kessler's special case, in which only one oxidizing agent and two reducing agents are present or *vice-versa*; the name "actor" is given to the oxidizing agent in cases of induced oxidation, and to the reducing agent in cases of induced reduction, while the "inductor" is the substance which reacts quickly with the actor, and accelerates or "induces" the reaction between the

[1] Pogg. Ann., **119**, 218 (1863).

[2] Liebig's Ann., **325** (1902).

[3] Kritische Studien über die Autoxydationsvorgänge. Braunschweig, 1903.

[4] Zeit. phys. Chem., **42**, 641 (1903).

[5] Ibid., **46**, 777 (1903).

[6] Chemical Statics and Dynamics, London, 1904.

actor and the third reagent, or "acceptor." The "induction factor" gives the number of equivalents of acceptor which enter into reaction while one equivalent of inductor is oxidized (or reduced) by the actor.

From the theoretical point of view, the simplest cases that come under Kessler's definition are those in which the induction can be explained by the known properties of an isolable product of the reaction between actor and inductor. In order to make sure that the explanation suggested is the true one, it is only necessary to study the two reactions: actor *plus* inductor, and product *plus* acceptor, separately, and compare them with the reaction which takes place in solutions containing actor, inductor, and acceptor together. This has been done by Harcourt and Esson[1] and by Bell[2] for the system H_2O_2, HI, $Na_2S_2O_3$; by Federlin[3] for the system $K_2S_2O_8$, HI, H_3PO_3; by Schilow[4] for the system $HBrO_3$, HBr, $HAsO_3$; and by Bowman[5] for the system $HBrO_3$, HI, $HAsO_3$. Cases like these belong demonstrably to the group of consecutive reactions, none of which were included by Kessler in his tables of examples; and it seems better to employ the term "induced reaction" only where no such obvious explanation is available.

It is possible, of course, to account for the remaining cases by assuming the temporary existence of some product which could take the place of the iodine or bromine in the foregoing examples, even where all attempts to isolate such a substance have failed. The first attempt to carry this idea through in detail was made by Manchot, whose views may be gained from the following much abridged free translation from his papers "On the Process of Oxidation"[6] and "On the Formation of Peroxides of Iron,"[7] published in 1902.

[1] Jour. Chem. Soc., **20**, 476 (1867).
[2] Jour. Phys. Chem., **7**, 61 (1903).
[3] Zeit. phys. Chem., **41**, 565 (1902).
[4] Ibid., **42**, 641 (1903).
[5] The results of this research will shortly be published.
[6] Liebig's Ann., **325**, 93 (1902).
[7] Ibid., **325**, 105 (1902).

Manchot's Peroxide Theory

"I was led to the following general theory of the processes of oxidation, which is completely contained in the sentence" *In every process of oxidation there is formed a primary oxide*[1] which in general has the character of a peroxide. The subsequent fate of the peroxide depends on the special circumstances of each case. The case that the final, isolable, product is identical with the peroxide seems to be the less common . . . . it is more usual for the peroxide to undergo decomposition before it can be isolated, giving up oxygen, which escapes as gas, or combines with other substances present (acceptors); among the latter may be included the substance itself which is undergoing oxidation (auto-acceptor).

"*The peroxide is formed direct* from the reagents, *intermediate states are passed over* . . . . and it is obviously only in special cases that the isolable product is more highly oxidized than the initial state (*e. g.*, ferrous—peroxide—ferric). The final state may be identical with the initial, or may be less oxidized than the latter, for instance the reduction of PbO_2 or MnO_2 by H_2O_2 in presence of acid (dioxide—peroxide—monoxide) . . . . and in some cases the product of decomposition may be the metal itself (Au from $AuCl_3$ by H_2O_2, etc.).

"This theory necessitates the assumption in the case of many elements, of stages of oxidation which are hitherto unknown. . . . . It brings the action of all oxidizing agents under a common point of view, but I wish to state emphatically that in my opinion it is of value chiefly because it incites to experimental investigation, and, without predicting the results of the latter, is able to modify itself in accordance with them. If in any case this should clearly be shown to be impossible, the theory must be laid aside."

Granting that the "primary product" of the oxidation of ferrous sulphate, for instance, is a peroxide of iron, the composition of the latter may be ascertained "by carrying

[1] The italics are the author's, throughout.

out the oxidation in presence of an acceptor, to which oxygen may be transferred from the peroxide. Many substances can act as acceptors, but for quantitative investigations only those of them are suitable which react fairly quickly with the ferric peroxide, so that the reduction of the peroxide is brought about *only* by the acceptor, the evolution of oxygen, or its transference to other substances (especially unused ferrous salt) being avoided. The action of the peroxide on the acceptor may be rendered more complete by increasing the concentration of the latter."

When a suitable acceptor has been found, it is only necessary to determine n, the number of atoms of oxygen absorbed by the acceptor for every Fe_2O_3 converted into Fe_2O_3; for the formula of the peroxide may be assumed to be Fe_2O_{3+n}.

$$2FeO \rightleftharpoons Fe_2O_{3+n} \rightleftharpoons Fe_2O_3 + nO$$

Thus, according to Manchot, every process of oxidation leads to the formation of a primary oxide, which in general has the character of a peroxide, and whose formula may be ascertained by determining the induction factor.

Luther and Schilow's Classification

Luther and Schilow[1] take a much broader view, and admit the existence of many types of induced reactions.

They begin by distinguishing cases of simple catalysis under conditions where the catalyzer is destroyed by independent reaction with the actor, from true copulated reactions; in the former the induction factor can be increased indefinitely by increasing the concentration of the acceptor; in the latter it reaches a limit which depends on the nature of the reaction "really" taking place in the solution.

The authors then discuss "the main question, namely, the methods of ascertaining the nature of the intermediate substance which brings about the copulation."

The upper limit, towards which the induction factor

[1] Zeit. phys. Chem., 46, 777 (1903).

tends as the concentration of the acceptor is increased, may be employed to determine the degree of oxidation of the intermediate compound, but gives no further information as to its formula, or as to the reagents from which it has been formed. In the authors' opinion, information on this point "can be obtained only by *suitable variation of the reagents;* reagents which are necessary for the formation of the intermediate substance must have certain properties, so that they can be varied (interchanged) only within definite limits; substances which can replace one another must in certain respects be *chemically analogous*, or at least be capable of *analogous chemical changes.* On the other hand, the substances which only react with the intermediate body may belong to widely different chemical classes, the single respect in which they must resemble one another being their ability to enter into an oxidation-reduction reaction with the (hypothetical) intermediate substance."

"Observation of the occurrence or non-occurrence of induction, when the reagents are systematically varied, therefore enables one—to a certain extent—to decide which of these substances plays a *specific rôle* in the reaction . . . . and leads to a classification of the cases of induction hitherto observed. The principle underlying the following attempt at such a classification, is the dependence of copulation on the specific nature of the three reagents—actor, inductor, acceptor."

In class A, the inductor is "specific," the other two "unspecific;" the intermediate body must therefore be a derivative of the inductor; in classes B and C, actor and acceptor respectively take the place of the inductor of class A. In class D, both acceptor and inductor are "specific," and the intermediate body must be regarded as a complex derived from both of them; classes E and F complete the series, inductor and actor, or acceptor and actor respectively, being "specific."

In the authors' attempt to distribute the known cases of induction among their six classes, the weakness of the "prin-

ciple" on which the classification rests becomes apparent. Ferrous salts, for instance, act as inductors in 15 reactions involving 7 actors and 9 acceptors—all are grouped in class A; but the 8 reactions in which SO_2 takes the part of inductor, and in which 6 actors and 4 acceptors are involved, are distributed among the remaining five classes. "This example shows how careful one must be in interpreting the phenomena of induction;" it also shows that much is left to individual opinion in the practical application of the authors' "principle" of classification; Luther and Schilow were quite clear on this point, "we consider our interpretations as in no case final."

A New Classification Based on Kinetic Measurements

A firmer basis for the classification may be secured by treating the problems of induction according to the methods of chemical kinetics; and comparing the rates at which the actor acts on inductor and acceptor taken each by itself, with the rates in solutions containing all three reagents together. Each case, of course, must be studied by itself, but when the effects of all the concentrations on the rates have been ascertained, a suitable hypothesis may be founded on the results of the measurements.

In the present almost total absence of experimental data, it would be premature to develope a detailed classification of the results that may be attained by future experimenters; it is sufficient to define the three classes into which all must fall, and to attract attention to an important ambiguity that must always attend attempts to assign a specific mechanism to any case of induction which falls under group II of the classification proposed.

The Three Classes

It is assumed that in every case the final products of the reactions in solutions containing all three reagents, are the same as the products of the reactions between actor and acceptor or actor and inductor separately. This excludes the obviously consecutive reactions referred to on page 10.

Class i.—The rate at which the inductor is acted on, and

the influence of the concentrations of the reagents on that rate, are unaffected by the presence and concentration of the acceptor. The reaction comes under the head of "Catalysis combined with destruction of the catalyzer," and as pointed out by Luther (page 12) the induction factor rises indefinitely with increase in concentration of the acceptor.

Class ii.—The rate at which the actor is destroyed, and the influence of the concentrations of the reagents on that rate, are independent of the presence and concentration of the acceptor; while the rate at which the inductor is acted on, though (necessarily) slower than in absence of the acceptor, is nevertheless affected by the concentrations of the reagents in the same manner as in the absence of the acceptor. The induction may be accounted for by assuming one of Manchot's peroxides or some other product of the action of actor on inductor. This is the only case which the peroxide hypothesis is sufficient to explain; it includes Luther's classes A, B and E.

Class iii.—The effect of the concentrations of the reagents on the rate at which the inductor is destroyed is changed by adding the acceptor. The intermediate formation of some derivative of the acceptor with actor or inductor may be assumed (Luther's D and F), or resort may be had to complicated hypotheses involving equilibria; the peroxide explanation, however, is clearly excluded.

The difficulties met with in carrying out the measurements necessary for this classification are principally those of chemical analysis: up to the present, however, only two cases of induction have been studied from this point of view, *viz.*: those in which the action of chromic acid on potassium iodide is accelerated by the simultaneous oxidation of ferrous sulphate or of arsenious acid, respectively. They afford typical examples of classes iii and ii.

Chromic Acid, Ferrous Sulphate, Potassium Iodide. Type of Class iii

This reaction is particularly interesting as it is one of those discussed by Manchot, who thought it afforded striking

evidence of the correctness of his theory. He considered the "primary product" of the reaction between chromic acid and ferrous sulphate to be a peroxide of the formula Fe_2O_5, which was instantaneously reduced to ferric oxide or its salts by the action of ferrous salts or of iodides. As this theory, which was subsequently adopted by Luther and Schilow, is totally at variance with the results of the kinetic measurements quoted below, it is worth while to recapitulate the arguments advanced in its support.

Manchot relied on his general theory of oxidation, outlined above (page 11), and on the observation that there is a "slight but distinct evolution of oxygen gas when ferrous sulphate is dropped into a concentrated solution of potassium bichromate in sulphuric acid;" he arrived at the formula of the peroxide by means of the induction factor. Theories of the induction based on a hypothetical ferro-hydriodic acid he dismissed on the ground that "potassium ferrocyanide[1] added to the system: chromic acid *plus* hydriodic acid, produces the same effect as ferrous sulphate, namely, sets iodine free; the liberation of iodine takes place a little more slowly, probably because the peroxide is more stable in this case; obviously there can be no talk of the formation of a ferro-hydriodic acid in this case, nor of similar complexes in the experiment on the decolorization of indigo, described below."

The considerations weighing with Luther and Schilow may be put shortly as follows: Ferrous salts act as inductors in numerous reactions involving actors and acceptors of the most varied character; these cases, therefore, all come under Group A (page 13), and are to be explained by assuming the primary formation of "an intermediate state of the inductor," that is, a peroxide of iron.

Miss Benson's measurements,[2] however, show that the effect of the concentrations of the reagents on the rate at which ferrous sulphate is oxidized by chromic acid are altogether

[1] See, however, Miss Benson's measurements: Jour. Phys. Chem., 7, 363 (1903).

[2] Jour. Phys. Chem., 7, 356 (1903).

changed by the addition of potassium iodide. In the absence of potassium iodide the rate is proportional to the square of the concentration of the ferrous salt, in its presence to the first power; in the absence of potassium iodide, to the second power of the concentration of the acid, in its presence, to the third or fourth power; in the absence of potassium iodide to the 1.4th or 1.8th power of the concentration of the bichromate, in its presence to the first power, while the effect of continuously increasing the concentration of the iodide is first to lower, then to increase the rate at which the ferrous sulphate was oxidized.

The case therefore comes under Class iii of page 15; and *it is quite impossible to assume*, with Manchot, and with Luther and Schilow, *that the reaction between ferrous sulphate and chromic acid in the presence of potassium iodide is essentially the same as in its absence.*

Chromic Acid, Arsenious Acid, Potassium Iodide. Type of Class ii

This reaction is not included in Luther and Schilow's tables, and is not mentioned by Manchot; the kinetic investigation, which has been carried out by Mr. R. E. De Lury,[1] establishes it as the type of Class ii.

Whether potassium iodide be present or not, the rate at which arsenious acid is oxidized by chromic acid is proportional to the concentrations of the arsenious acid and bichromate, and to the 1.4th power of that of the acid. When potassium iodide is added, iodine is set free; and as the concentration of the iodide is increased the rate of liberation of iodide increases and the rate of oxidation of arsenious acid decreases, until the latter falls to one-third the rate in the absence of iodide. When this point has been reached, two equivalents of iodine are liberated for each equivalent of arsenious acid oxidized, and further increase in the concentration of the iodide has no effect on the rates. Throughout, the rate at which the chromic acid is reduced by the mixture

[1] Trans. Roy. Soc., Canada, May, 1905.

of iodide and arsenious acid is the same as though the arsenious acid were present alone.

Thus, in contrast to the case of induction studied by Miss Benson, *the reaction involving the reduction of chromic acid is essentially the same whether iodide be added or not*; it may therefore be accounted for by assuming that a (hypothetical) peroxide of arsenic is the primary product of the reaction whose rate is measured, and that this peroxide is immediately reduced to arsenic acid by either potassium iodide or arsenious acid (Manchot's hypothesis).

Alternative Mechanisms for Reactions of Class ii

From what precedes, it is clear that a study of the rates at which inductor and acceptor are acted on by the oxidizing agent (actor) is sufficient to assign each case studied to one of three classes; and in particular, that cases of induction which can be explained on Manchot's hypothesis may be distinguished by this means from those which can not.

The results of the rate measurements, on the other hand, may often be explained equally well by several different hypothetical mechanisms, within the same group. Mr. De Lury's experiments with chromic acid, arsenic, and potassium iodide, for instance, may be accounted for by assuming either As_2O_9, Cr_2O_5, or their hydrates, or some Cr–As compound of a suitable state of oxidation, as the primary product of the action of chromic acid on arsenious acid.

The method of "suitable variation of the reagents" leads to no definite conclusion as to which of these assumptions is the best. True, the reaction between chromic acid and iodides is induced by ferrous salts and by tartaric acid as well as by arsenious acid, which seems to point to the chromic acid as the "specific" and the arsenic as the "unspecific" reagent, and thus to support the Cr_2O_5 hypothesis; the As_2O_9 theory, however, is suggested by the occurrence of numerous reactions in which arsenious acid plays the part of inductor, and although iodides are not mentioned as acceptors in any of the cases recorded in Luther's tables, this may be due to

the difficulty of finding another oxidizing agent which (like chromic acid) acts on arsenic quicker than on potassium iodide.

It is possible, on the other hand, that further rate measurements may lead to the adoption of one of the three theories rather than the others; although, as all three lead to the same conclusions with regard to the induction just studied, this might at first sight seem impossible.

For example, the fact that in dilute solutions the rate of oxidation of potassium iodide by chromic acid[1] is proportional to the concentrations of the iodide and bichromate, may be accounted for by assuming the reaction

$$H_2CrO_7 + HI = HOI + H_2Cr_2O_6$$

in which the hypothetical $H_2Cr_2O_6$ (a hydrate of the Cr_2O_5 of page 18) is taken as "primary product." But if this view of the reaction between chromic and hydriodic acids be combined with the Cr_2O_5 explanation of the induction by arsenious acid, it follows that hydriodic acid must act as inductor to the reaction between arsenious and chromic acids, that the two reactions must be reciprocally inductive in fact; and it is even possible to calculate the effects of the concentrations on the rates and on the induction factor in one case from a knowledge of the other.

As the rates at which chromic acid oxidizes hydriodic and arsenious acids, respectively, are different functions of the concentrations of the acid, it may be possible to increase the former and decrease the latter sufficiently to render these relations accessible to experimental investigation. Such experiments, if carried out, would remove one more degree of freedom from the imagination when inventing "mechanisms" to explain the phenomena of chemical induction.

Summary

The methods hitherto proposed for classifying cases of chemical induction are unsatisfactory.

A new classification is proposed, based on kinetic measure-

[1] Jour. Phys. Chem., 7, 239 (1903).

ments. According to this, the induced reactions are divided into three classes: (i) cases of catalysis combined with destruction of the catalyser, (ii) cases in which the reaction between actor and inductor is the same whether acceptor be present or no, (iii) cases in which it is not.

Only two induced reactions have as yet been studied from this point of view; they furnish typical examples of classes ii and iii.

Reactions of class ii can be explained equally well by several different hypothetical mechanisms (including Manchot's peroxide hypothesis), all of which predict the same kinetic relations. The choice may be narrowed, however, by further kinetic experiments.

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THE RATE OF OXIDATION OF ARSENIOUS ACID BY CHROMIC ACID.

BY RALPH E. DE LURY

The following measurements together with those on the rate of oxidation of iodide by chromic acid[1] constitute a necessary preliminary investigation to the study of the rates of the reactions in solutions containing arsenious acid, iodide, bichromate and sulphuric acid.[2]

In all of these experiments the concentration of the arsenious acid was small and the sulphuric acid and potassium bichromate concentrations relatively large, so that the results might be directly comparable with the measurements in which iodide was present. It was consequently possible to consider the concentrations of the sulphuric acid and bichromate as constant in the experiments of each table.

Method of Experimenting

A supply of distilled water and dilute solutions of potassium bichromate, sulphuric acid and arsenious acid were kept at 0° *C* in a thermostat. The bichromate and sulphuric acid and some of the water were measured into a beaker clamped down in the bath; the arsenious acid mixed with the rest of the water necessary to make up the required total volume, was thrown into the beaker from a large test-tube, the reacting mixture violently stirred and the time noted. To stop the reaction a quantity of ammonium bicarbonate solution more than sufficient to neutralize the acid present was added to the beaker and the contents were thoroughly stirred. The residual arsenious acid was then determined by titration with volumetric iodine and arsenious acid.

Solutions Employed

The following stock solutions were prepared:

Potassium Bichromate, $K_2Cr_2O_7$, 0.1 *F*, or 0.6 *N*, prepared

[1] De Lury: Jour. Phys. Chem., 7, 239 (1903).

[2] Ibid., immediately following the present paper.

by dissolving 58.9 grams of the pure salt in 2 liters of distilled water.

Sulphuric Acid, H_2SO_4, 0.967 *N*, standardized gravimetrically with barium.

Arsenious Acid, As_2O_3, 0.025 *F*, or 0.1 *N*, prepared by dissolving 9.90 grams of pure "lump white arsenic" in hot water and diluting to 2 liters with distilled water; before use the solution was diluted to ten times its volume with boiled distilled water (to prevent slow oxidation by oxgyen).

Iodine, approximately 0.1 *N*, prepared by dissolving resublimed iodine in potassium iodide solution and diluting. For titrating, this solution was diluted to ten times its volume and compared frequently with the volumetric arsenious acid solution.

Ammonium Bicarbonate, "restrainer," prepared by passing carbon dioxide into a saturated solution of commercial ammonium carbonate, diluting with its own volume of water and again saturating with carbon dioxide.

Starch Solution, "indicator," prepared frequently by dissolving a gram or two of starch in 500 *cc* of boiling water, cooling and allowing to settle.

Explanation of the Tables

After *Cr* and *Ac* at the head of the tables are given the amounts expressed in 10^{-5} gram-formula-weights (*i. e.*, in *cc* of 0.01 solution) of $K_2Cr_2O_7$ and H_2SO_4 respectively; after *As* the amount of As_2O_3, the unit being 0.25×10^{-5} gram-formula-weights (*i. e.*, 1 *cc* of 0.01 *N* solution); after *Vol.* is given the volume of the reacting mixture in cubic centimeters. The constant k is defined by the equation, $k = \frac{1}{t}.\log._{10}\frac{As}{As - x}$, where x is the amount (expressed in *cc* of 0.01 *N* solution) of arsenious acid oxidized in t minutes. After *Avg.* at the end of the tables is given the average of the constants; in taking the average, bracketed numbers were omitted.

TABLE I

As, 9.94; *Cr*, 149; *Ac*, 484; *Vol.*, 500

t	*As* − *x*	*x*	*k*
2	7.54	2.40	0.060
3	6.53	3.41	0.061
4	6.04	3.90	0.054
5	5.20	4.74	0.056
7	3.91	6.03	0.058
		Avg.	0.058

TABLE II

As, 9.94; *Cr*, 298; *Ac*, 484; *Vol.*, 500

t	*As* − *x*	*x*	*k*
1	7.51	2.43	0.122
2	6.05	3.89	0.108
3	5.00	4.94	0.100
4	3.93	6.01	0.108
		Avg.	0.110

TABLE III

As, 9.94; *Cr*, 447; *Ac*, 484; *Vol.*, 500

t	*As* − *x*	*x*	*k*
1	6.46	3.48	0.187
2	4.54	5.40	0.170
		Avg.	0.178

TABLE IV

As, 4.95; *Cr*, 149; *Ac*, 484; *Vol.*, 500

t	*As* − *x*	*x*	*k*
1	4.45	0.50	(0.046)
2	3.92	1.03	0.051
3	3.44	1.51	0.053
4	3.02	1.93	0.054
5	2.72	2.23	0.052
		Avg.	0.052

TABLE V

As, 9.94; *Cr*, 149; *Ac*, 968; *Vol*, 500

t	*As* − *x*	*x*	*k*
1	6.61	3.33	(0.177)
1.5	5.56	4.38	0.168
2	4.70	5.24	0.163
2.5	3.93	6.01	0.161
3	3.17	6.77	0.166
		Avg.	0.164

TABLE VI

As, 9.94; *Cr*, 149; *Ac*, 725; *Vol.*, 500

t	*As* − *x*	*x*	*k*
1	7.58	2.36	(0.118)
1.5	6.79	3.15	0.110
2	5.96	3.98	0.111
2.5	5.40	4.54	0.106
3	4.83	5.11	0.105
4	3.80	6.14	0.104
		Avg.	0.107

In the measurements of Tables I–VI the residual arsenious acid was not always titrated immediately after adding the restrainer; this introduced an error due to oxidation of arsenious acid in alkaline solution.[1] In the measurements of Tables VII–XVI the arsenious acid was titrated with iodine

[1] Kessler: Pogg. Ann., 113, 142 (1861). In an average case (Table XIV), it was found that about 0.05 *cc* of 0.01 *N* arsenious acid solution was oxidized in one minute after adding the restrainer.

in the ice bath immediately after stopping the reaction; to make the end-point distinct, a light and reflector and beakers coated with white enamel were used. The constants of these tables are more uniform than those of the above six tables.

TABLE VII (under CO_2)

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	8.77	1.23	0.0114
10	7.67	2.33	0.0115
15	6.69	3.31	0.0116
20	5.90	4.10	0.0115
		Avg.	0.0115

TABLE VIII

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	8.79	1.21	0.0112
10	7.66	2.34	0.0116
15	6.72	3.28	0.0115
20	6.01	3.99	0.0111
25	5.20	4.80	0.0114
30	4.75	5.25	(0.0108)
		Avg.	0.0114

TABLE IX

As, 20.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	17.32	2.68	0.0121
10	15.27	4.73	0.0117
15	13.50	6.50	0.0114
20	11.95	8.05	0.0112
		Avg.	0.0116

TABLE X

As, 5.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	4.37	0.63	0.0117
10	3.84	1.16	0.0115
15	3.32	1.68	0.0112
20	2.97	2.03	0.0113
25	2.59	2.41	0.0114
30	2.29	2.71	0.0113
		Avg.	0.0114

TABLE XI

As, 10.00; *Cr*, 20; *Ac*, 484; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	6.83	3.17	0.0332
10	4.83	5.17	0.0316
14	3.71	6.29	0.0307
		Avg.	0.0318

TABLE XII

As, 5.00; *Cr*, 20; *Ac*, 484; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	3.48	1.52	0.0315
10	2.47	2.53	0.0306
15	1.77	3.23	0.0301
20	1.30	3.70	0.0293
25	0.96	4.04	0.0287
		Avg.	0.0300

TABLE XIII

As, 10.00; *Cr*, 40; *Ac*, 242; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	7.77	2.23	0.0219
10	6.07	3.93	0.0217
15	4.78	5.22	0.0214
		Avg.	0.0217

TABLE XIV

As, 5.00; *Cr*, 40; *Ac*, 242; *Vol.*, 300

t	*As* − *x*	*x*	*k*
5	4.05	0.95	(0.0183)
10	3.24	1.76	0.0188
14	2.55	2.45	0.0209
15	2.51	2.49	0.0202
20	1.92	3.08	0.0208
25	1.76	3.24	(0.0181)
30	1.37	3.63	0.0188
		Avg.	0.0200

TABLE XV

As, 10.00; *Cr*, 20; *Ac*, 121; *Vol.*, 300

t	*As* − *x*	*x*	*k*
10	9.00	1.00	0.0046
20	8.20	1.80	0.0043
22.5	7.99	2.01	0.0043
30	7.38	2.62	0.0043
		Avg.	0.0044

TABLE XVI (*10° C*)

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As* − *x*	*x*	*k*
10	7.15	2.85	0.0146
15	6.10	3.90	0.0146
20	5.18	4.82	0.0143
		Avg.	0.0144

The oxygen of the air, while it affects the oxidation of arsenite in alkaline solution, has no effect on the oxidation of arsenious acid by chromic acid. This is seen by comparing Tables VII and VIII. The measurements of VII were made, using solutions free from air and protecting the reacting mixture with carbon dioxide; those of VIII were made, taking no precautions to exclude air. The constants and *As*–*x* readings agree closely.

I further satisfied myself that arsenic acid of the concentration formed in the experiments has no effect on the rate of oxidation of arsenious acid.

Discussion of the Results

Effect of the Arsenious Acid.—The fair constancy of *k* throughout the tables, more particularly in Tables VII–XVI where special precautions were taken, leads to the conclusion that the rate of oxidation of arsenious acid by chromic acid is

proportional to the first power of the concentration of the arsenious acid; conclusive proof of this is furnished by the fact that k is unaffected by changing the concentration of the arsenious acid (Tables I and IV; VII, VIII and IX; XI and XII).

Effect of the Bichromate.—Doubling the concentration of the bichromate nearly doubles the constant, or halves the time necessary for the oxidation of the same amount of arsenious acid (Tables I and II; VII, VIII and XIII; X and XIV). Trebling Cr trebles k or divides by three the time necessary for the oxidation of a fixed amount of arsenious acid (Tables I and III). The rate of oxidation of arsenious acid is thus nearly proportional to the first power of the concentration of the bichromate. This deviation from an exact first power may be attributed to incomplete dissociation of $H_2Cr_2O_7$. To account for the fall in the constant it is necessary to assume that the dissociation of the chromic acid in mixture VIII is about 7 percent greater than in XIII.[1]

Effect of the Sulphuric Acid.—If the concentration of the sulphuric acid be doubled the constant is nearly trebled, or the time needed to oxidize the same amount of arsenious acid is divided by three (Tables I and V, VII, VIII and XI). The results of Table VI are in accord with this. The rate may thus be set proportional to the $1.4th$ or $1.5th$ power of the concentration of the sulphuric acid. The deviation from a sharp second power is probably due to the influence of the hydrogenion on the dissociation of the arsenious acid; it is quite possible that arsenious acid in more than one form (ions or undissociated acid) reacts with chromic acid, and the rates of these reactions involve different powers of the concentration of the hydrogenion, the resultant power being the $1.4th$ in the above experiments.

Effect of the Temperature.—For an increase of 10° C in the temperature the constant is increased from 0.0114 to 0.0144 (Tables VIII and XVI); that is, the rate is increased only 26 percent, a very low temperature effect indeed.

[1] See also Jour. Phys. Chem., 7, 248 (1903).

The experimental results of this investigation are summarized in Table XVII. K is defined by the equation (*Vol.* 300 *cc.*),

$$\frac{dx}{dt} = K(As - x).Cr^{0.9}.Ac^{1.4},$$

and hence

$$K = \frac{2.30\,k}{Cr^{0.9}.Ac^{1.4}} \cdot \left\{\frac{Vol}{300}\right\}^{2.3}.$$

It will be seen that the value of K is fairly constant throughout.

TABLE XVII

Table	*As*	*Cr*	*Ac*	*Vol.*	*k*	K × 10⁸
I	9.94	149	484	500	0.058	84
II	9.94	298	484	500	0.110	85
III	9.94	447	484	500	0.178	95
IV	4.95	149	484	500	0.052	75
V	9.94	149	968	500	0.164	89
VI	9.94	149	726	500	0.107	87
VII	10.00	20	242	300	0.0115	82
VIII	10.00	20	242	300	0.0114	82
IX	20.00	20	242	300	0.0116	83
X	5.00	20	242	300	0.0114	82
XI	10.00	20	484	300	0.0318	86
XII	5.00	20	484	300	0.0300	81
XIII	10.00	40	242	300	0.0217	83
XIV	5.00	40	242	300	0.0200	77
XV	5.00	20	121	300	0.0044	83

Summary

The rate of oxidation of arsenious acid (dilute solutions) by bichromate and sulphuric acid, is proportional to the first power of the concentration of the arsenious acid, the 0.9*th* power of the concentration of the bichromate and the 1.4*th* power of the concentration of the sulphuric acid, that is,

$$\frac{dx}{dt} = K(As - x).Cr^{0.9}.Ac^{1.4}.$$

The effect of temperature on this reaction is unusually small; for an increase of 10° *C* the rate is increased only 26 percent.

University of Toronto,
May, 1905

THE INDUCTION BY ARSENIOUS ACID OF THE REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS

BY RALPH E. DE LURY

It has long been known that the process of oxidation in solution can often be hastened by the presence of a small quantity of some easily oxidizable substance. This phenomenon is called *induced oxidation*: the name *acceptor* is given to the substance whose oxidation is accelerated and the reagent causing the acceleration is called the *inductor*. Ferrous salts, arsenious acid and nitric oxide act as inductors and iodide as acceptor for the oxygen of chromic acid.

About the middle of the last century many cases of induced oxidation, occurring chiefly in the development of methods of analysis, were noted and classified by Schönbein, Kessler and others. By selecting various combinations of reducing and oxidizing agents the number of similar cases might be multiplied indefinitely. Many of these cases have been studied qualitatively and to a certain degree quantitatively, and the attempts to explain the results of these investigations have led to the development of the *peroxide theory* so ably championed by Manchot.[1]

The peroxide theory is based on a considerable amount of qualitative and some quantitative data, and on the fact that some peroxides are known to be formed in the process of oxidation, such as hydrogen peroxide and benzoyl hydroperoxide: these peroxides may be regarded as the primary products of the oxidation of hydrogen and benzaldehyde respectively.

However, if a *non-isolable* peroxide, regarded as the cause of induced oxidation, be formed, its formation can be ascertained only by a careful study of the rates of all the reactions involved, since it is as an explanation of these rates

[1] Lieb. Ann., 325, 95 (1902).

that the peroxide theory is advanced. This obvious method of attacking the problem has been neglected, no doubt on account of the difficulties of analysis which such a method in general presents; hence the quantitative investigation of such cases has been chiefly confined to the measurement of the ratio of the amounts of inductor and acceptor oxidized when the reaction is complete.[1] Such a method will often give the oxidizing value of the intermediate product but the results are not reliable or sufficient.

The only case of which I am aware to which the method of studying all the rates involved has been applied as yet, is the reactions in solutions containing chromic acid, iodide and ferrous salt[2] investigated by Miss C. C. Benson, and curiously enough the results are not in accord with the peroxide theory.

In the present paper I communicate the results of measurements of the rates of the reactions in solutions containing chromic acid, iodide and arsenious acid and am able to show that the assumption of the formation of a peroxide explains the induction in this case. The rates of oxidation of iodide[3] and of arsenious acid[4] by chromic acid have already been studied by myself.

Plan of the Investigation

In solutions containing potassium iodide, arsenious acid, potassium bichromate and sulphuric acid the following reactions may occur:

A. Oxidation of the iodide by chromic acid,

$$9KI + K_2Cr_2O_7 + 7H_2SO_4 = 3KI_3 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O,$$

[1] Manchot: loc. cit.; Schilow: Zeit. phys. Chem. **42**, 641 (1903).
[2] Jour. Phys. Chem., 7, 356 (1903).
[3] Ibid., 7, 239 (1903).
[4] Ibid., 11, 47 (1907).

whose rate at o° *C*, may be represented[1] approximately by the kinetic equation:[2]

$$\frac{dI_3}{dt}(c) = Ric = 1 \times 10^{-12}.Cr.(Ac)^2.\left[KI + 0.002(KI)^2\right] \qquad (1)$$

B. Oxidation of arsenious acid by chromic acid,

$$3As_2O_3 + 2K_2Cr_2O_7 + 8H_2SO_4 = 3As_2O_5 + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 8H_2O.$$

In the absence of potassium iodide the rate of this reaction at o° *C*, may be represented by the equation:[3]

$$\frac{d\overset{v}{As}}{dt}(c) = Rac = 83 \times 10^{-8}.As.(Cr)^{0.9}.(Ac)^{1.4} \qquad (2)$$

C. Oxidation of the iodide by arsenic acid formed in the reaction,

$$6KI + As_2O_5 + 2H_2SO_4 = 2KI_3 + As_2O_3 + 2K_2SO_4 + 2H_2O,$$

and the rate of this reaction at o° *C*, may be represented[4] thus:

$$\frac{dI_3}{dt}(a) = Ria = 4 \times 10^{-12}.\overset{v}{As}.KI.Ac \qquad (3)$$

---

[1] *KI*, *Cr* and *Ac* denote the amounts of potassium iodide, potassium bichromate and sulphuric acid respectively, expressed in 10^{-5} gram-formula-weights (i. e. in *cc*. of 0.01 *F* solution): the same unit as employed in the measurements on the rate of oxidation of iodide by chromic acid (*loc. cit.*). *As* and $\overset{v}{As}$ denote respectively the amounts of arsenious acid and arsenic acid expressed in 0.25×10^{-5} gram-formula-weights (i. e. in *cc*. of 0.01 *N* solution); this unit is selected in order to facilitate comparison between the iodine and arsenious acid readings in the Tables which follow. I_3 denotes the "free iodine" in 0.5×10^{-5} gram-formula-weights (i. e. in *cc*. of 0.01 *N* solution). The letter *R* denotes rate; *Ric* denotes the rate of oxidation of iodide by chromic acid; *Rac* denotes the rate of oxidation of arsenious acid by chromic acid, etc. In the subscripts *ic*, *ac*, etc. the letters *i*, *a*, *c*, suggest iodide (or triiodide), arsenious acid (or arsenic acid), and chromic acid respectively: the letter which goes first denoting the substance oxidized and the second letter the substance oxidizing.

The constants are calculated for a volume of 300 *cc*.

[2] De Lury: loc. cit.

[3] The paper just preceding the present paper.

[4] Roebuck: Jour. Phys. Chem., 6, 365 (1902). In concentrated solutions the indices of the power of *KI* and *Ac* are greater than 1.

D. Oxidation of the arsenious acid by the triiodide formed in the reaction,

$$As_2O_3 + 2KI_3 + 2K_2SO_4 + 2H_2O = As_2O_5 + 6KI + 2H_2SO_4$$

whose rate at o° *C*, is expressed by:[1]

$$\frac{dAs}{dt}^{v}(i) = -\frac{dI_3}{dt}(a) = Rai = 1 \times 10^{-6}.I_3.As.(KI)^{-2}.(Ac)^{-1} \quad (4)$$

E. Oxidation of the iodide due to the influence of the arsenious acid; the symbol *Rip* denotes the rate of this reaction.[2]

In order to simplify the study of the rate of reaction *E* the concentrations of the reagents were selected so as to reduce the rates of reactions *A*, *C* and *D* as much as possible. Of these, reaction *C* (*Ria*) gave no trouble at all since the rate constant is very small and no arsenic acid was present except that formed in reactions *B* (*Rac*) and *D* (*Rai*). The loss of I_3 by reaction *D* could not be prevented by high concentrations of *KI* and *Ac* without unduly increasing *Ric*, and in the end it was found necessary to remove the iodine as soon as it was liberated by the use of thiosulphate (see page 58).

Thus in my experiments *Ria* and *Rai* were negligibly small, and therefore,

$$\frac{dAs}{dt}^{v} = Ra = Rac + M^3 \quad (5)$$

$$\frac{dI_3}{dt} = Ri = Ric + Rip \quad (6)$$

and *Ric* being determined by blank experiments *Rip* is obtained by difference.

EXPERIMENTAL PART

It was necessary to determine the quantities of iodide and arsenious acid oxidized at any stage of the reaction. Three methods of analysis were tried.

First Method.—When a suitable interval had elapsed the

[1] Roebuck: Loc. cit.

[2] *p*, for peroxide in anticipation of the theory (see p. 78).

[3] *M* is the modification in *Rac* due to the iodide (see p. 73).

concentration of the acid was reduced by addition of sodium bicarbonate, the iodine quickly titrated with sodium thiosulphate, excess of ammonium bicarbonate added and the residual arsenious acid titrated with iodine. This method was not successful.

Second Method.—After the reaction had proceeded for some time excess of ammonium bicarbonate was added and the arsenious acid titrated with iodine. In a duplicate experiment after the same interval, a measured quantity of 0.002 *N* thiosulphate solution, slightly in excess of the iodine present, was thrown into the reacting mixture, with violent stirring just before the ammonium bicarbonate which served as restrainer. Starch was then added and the arsenious acid and residual thiosulphate titrated with iodine, the iodine added being the sum of the arsenious acid and a *function* of the remaining thiosulphate. From these two measurements the arsenious acid oxidized and the iodine present could be determined if this function were known. Experiments showed that it depended on so many variables that no reliable determinations could be made, and the method was abandoned.

Third Method.—In the end a modification of Harcourt and Esson's compensation method was found to serve, and was adopted in all the measurements of this paper. The details of the method are as follows:

Method of Making the Measurements

Distilled water and dilute solutions of potassium bichromate, sulphuric acid, potassium iodide and arsenious acid were kept at 0° *C* in a thermostat. The bichromate, sulphuric acid and water were mixed in a beaker coated on the outside with white enamel. In a large test-tube the iodide and arsenious acid were mixed and a little starch solution added. At a suitable time the contents of the test-tube were thrown into the beaker with violent stirring, and a stopwatch set going by pressure of the foot.

Over the beaker was clamped a 10 *cc* burette from which 0.01 *N* sodium thiosulphate solution was added drop by drop

as the reaction proceeded, care being taken to keep the solution in the beaker as near as possible free from both iodine and thiosulphate. A number of readings of the burette were made during each experiment, and finally after a definite interval the reaction was stopped with excess of ammonium bicarbonate, and the residual arsenious acid titrated immediately[1] with iodine.

To test the method of analysis the measurements recorded in Tables I, II and III were made. In these tables, "*yellow*" denotes "slight excess of thiosulphate," and "*green*" denotes "slight excess of iodine," that is, just enough to keep the reacting mixture bluish green with the starch present; "*close*" means "as near as possible free from both thiosulphate and iodine."

TABLE I

As, 10.00; *KI*, 9.8; *Cr*, 20; *Ac*, 484

Minutes	*cc* thiosulphate
5.1	1.59 *yellow*
5.1	1.31 *close*
5.1	1.09 *green*

TABLE II

As, 10.00; *KI*, 245; *Cr*, 20; *Ac*, 242

Minutes	*cc* thiosulphate
9.5	2.00 *yellow*
9.5	2.00 *close*
9.6	2.00 *green*

TABLE III

As, 10.00; *KI*, 98; *Cr*, 20; *Ac*, 242

cc thiosulphate	*yellow* *Minutes*	*close* *Minutes*	*green* *Minutes*
0.50	3.2	3.5	3.3
1.00	6.0	6.2	6.2
1.50	9.0	9.1	8.8
2.00	11.9	12.0	12.0

In Table I where the concentration of the iodide was low the amount of thiosulphate needed to neutralize the iodine liberated in a fixed interval, depends on the method of working. This is due to the absorption of iodine by arsenious acid, and as the rate of this reaction[2] is inversely proportional

[1] To prevent oxidation of the arsenite in the alkaline solution of chromate and oxygen.

[2] See equation (4).

to the square of the concentration of the iodide, the difference in the thiosulphate readings becomes less when the concentration of the iodide is increased and disappears when the iodide concentration is equal to (or greater than) ten times the concentration of the arsenious acid (Tables II and III). The fact that in these last two tables, the readings made when the mixture was "*yellow*" and "*green*" are the same is proof that the oxidation of thiosulphate by chromic acid[1] is negligible. In those of my measurements where the concentration of the iodide was small, I was careful to keep the reacting mixture slightly "*yellow*" until near the end of the interval desired; this involved an approximate knowledge of the rate at which the iodine was being liberated and in some cases necessitated the duplication of the experiments.

A number of blank experiments carried out for the purpose, showed that neither the oxygen of the air, nor the arsenic acid[2] and tetrathionate[3] formed in the reaction, affected the rates.

Solutions Employed

In addition to the solutions, $K_2Cr_2O_7$, 0.1 F or 0.6 N; H_2SO_4, approximately 0.1 N; As_2O_3, 0.025 F or 0.1 N; ammonium bicarbonate and starch, employed in the measurements on the rate of oxidation of arsenious acid by chromic acid, a solution of potassium iodide 0.098 F (standardized by silver) and approximately 0.01 N solutions of thiosulphate and iodine (standardized by comparison with the arsenious acid), were used.

Explanation of the Tables

After *KI*, *Cr* and *Ac* at the head of the tables are given the amounts, expressed in 10^{-5} gram-formula-weights (*i. e.*, in *cc* of 0.01 F solution) of *KI*, $K_2Cr_2O_7$ and H_2SO_4 respectively

[1] See Bell: Jour. Phys. Chem., 7, 61 (1903).

[2] See equation (3) above, et seq.

[3] The concentration of the tetrathionate is not large enough to cause any error due to decomposition in the alkaline solution during the short interval between adding the bicarbonate and the completion of the titration.

(the same unit as employed in the measurements of the oxidation of iodide); after *As*, the amount of As_2O_3, the unit being 0.25×10^{-5} gram-formula-weights (*i. e.*, 1 *cc* 0.01 *N* solution), this unit is selected so as to facilitate comparison between the iodine and arsenious acid readings.

Under *t* are entered the durations of the reaction in minutes. Under *h* are given the amounts of thiosulphate ("*hypo*"), added from the small burette during the reaction expressed in *cc* of 0.01 *N* solution. Under *As–x'* are entered the amounts of arsenious acid remaining unoxidized after *t* minutes, expressed in *cc* of 0.01 *N* solution; *x'* thus represents the amount of arsenious acid oxidized: this symbol is used only when iodide is present in the reacting mixture. The symbol *x* denotes the amount of arsenious acid oxidized in the absence of iodide.

Under *ic* in Table XXI are given the amounts of iodine (in *cc* of 0.01 *N* solution) liberated by the oxidation of iodide in the absence of arsenious acid. The experiments were carried out just like those in which arsenite was present (page 58), and the *ic* readings were obtained from the readings of the small thiosulphate burette. The numbers under *ic* in Tables IV–X and XII–XX were obtained from these by interpolation. In Table XI where the reaction was allowed to proceed until the arsenious acid was completely oxidized, the numbers under *ic* (*calc*) were calculated from the equation, $ic(calc) = 0.60 \frac{t}{5} \cdot \frac{20 \times 6 - 0.5(h + x')}{20 \times 6}$, thus allowing for the decrease in the concentration of the bichromate.

In all of the experiments the initial volume was as near as possible $300 - \frac{h}{2}$ *cc*, so that the average volume during the reaction was 300 *cc*. The temperature was always 0° *C* except in Table XX and in one series of Table XXI where the temperature was 10° *C*.

The difference between the amounts of iodine liberated in the presence and absence of arsenious acid is entered under

h—ic. The constant, k', is defined by the equation, $k' = \frac{1}{t} \cdot \log_{10} \frac{As}{As - x'}$. When no iodide is present k' becomes k of the tables on the oxidation of arsenious acid by chromic acid, and at the same time x' becomes x of those tables (i. e., k and x are the limiting values of k' and x' when $KI = 0$).

In Tables V–IX, *Ra* and *Rip* (see page 56) represent the rates of oxidation of arsenious acid, and of iodide in the presence of arsenious acid after correcting for the direct action of chromic acid. Since the concentrations of the bichromate and sulphuric acid are so large that they may be regarded as constant, the rate, *Ra*, may be calculated by the equation:

$$Ra = 2.30k' . As$$

Rac is the limiting value of *Ra* when $KI = 0$.

A rough approximation to the rate, *Rip*, is given by the quotient, $\frac{h - ic}{t}$; in this expression, however, the decrease in the concentration of the arsenious acid during the reaction is neglected. In the experiments of Tables V–IX this decrease is at most 25 *percent*, and hence the average amount of arsenite present during the interval is closely represented by As—$0.5x'$. On page 74 I show that the rate is proportional to the concentration of the arsenious acid, and have therefore employed the following expression for calculating the values of *Rip*:

$$Rip = \frac{h - ic}{t} \cdot \frac{As}{As - 0.5x'}.$$

TABLE IV

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 121; *t*, 22.5

n	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
30	1.60	9.25	0.69	0.18	1.42	2.06	0.0014
40	1.75	9.30	0.64	0.31	1.44	2.25	0.0013
50	1.93	9.26	0.68	0.52	1.41	2.07	0.0013
60	2.03	9.33	0.61	0.70	1.33	2.18	0.0012
70	2.25	9.28	0.66	0.90	1.35	2.04	0.0013
80	2.40	9.27	0.67	1.10	1.30	1.94	0.0013

TABLE V

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *t*, 10

n	*h*	$As-x'$	*ic*	$r=\frac{h-ic}{x'}$	*k'*	*Rip*	*Ra*	*Rip* + *Ra*
0	—	—	—	—	—	0.000	0.263	0.263
1	0.43	7.97	0.01	0.21	0.0096	0.046	0.221	0.267
2	0.70	8.32	0.02	0.42	0.0077	0.073	0.178	0.251
4	1.33	8.79	0.04	1.12	0.0053	0.137	0.122	0.259
6	1.53	8.81	0.06	1.30	0.0052	0.156	0.120	0.276
8	1.60	8.86	0.08	1.41	0.0050	0.160	0.116	0.276
10	1.74	9.00	0.10	1.75	0.0043	0.172	0.099	0.271
10	1.98	9.16	0.10	(2.41)	0.0036	0.195	0.083	0.278
12	1.80	9.07	0.14	1.91	0.0040	0.173	0.092	0.265
15	1.83	9.12	0.19	2.00	0.0037	0.170	0.085	0.255
20	1.88	9.00	0.26	(1.71)	0.0043	0.169	0.099	0.268
30	2.00	9.18	0.43	2.07	0.0035	0.163	0.081	0.244
30	2.17	9.12	0.43	2.12	0.0037	0.182	0.085	0.267
40	2.24	9.25	0.63	2.33	0.0031	0.167	0.071	0.238
50	2.58	9.29	0.95	(2.51)	0.0029	0.168	0.067	0.235
60	2.70	9.18	1.15	2.04	0.0035	0.160	0.081	0.241
70	3.02	9.25	1.45	2.27	0.0031	0.162	0.071	0.233
80	3.30	9.26	1.75	2.26	0.0031	0.160	0.071	0.231

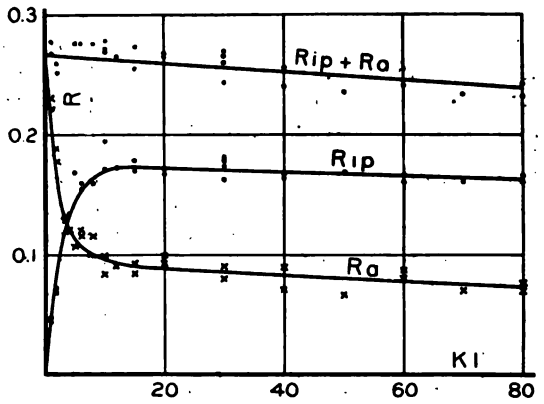

Fig. 1 (Cf. Tables V and VI)

NOTE.—In Figs. 1–4, the unit in which *KI* is represented is 9.8×10^{-5} gram-formula-weights.

TABLE VI

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *t*, 15

n	*h*	$As-x'$	*ic*	$r=\frac{h-ic}{x'}$	*k'*	*Rip*	*Ra*	*Rip* + *Ra*
0	—	—	—	—	—	0.000	0.263	0.263
1	0.63	7.03	0.01	0.21	0.0100	0.047	0.230	0.277
2	0.95	7.48	0.02	0.38	0.0082	0.069	0.189	0.258
3	1.87	8.15	0.03	1.03	0.0057	0.134	0.131	0.265
5	2.40	8.46	0.05	1.59	0.0047	0.169	0.108	0.277
6	2.27	8.33	0.06	(1.37)	0.0051	0.160	0.117	0.277
10	2.52	8.56	0.15	1.68	0.0043	0.170	0.099	0.269
15	2.72	8.63	0.28	1.86	0.0041	0.179	0.094	0.273
20	2.78	8.63	0.39	1.82	0.0041	0.171	0.094	0.265
30	3.15	8.67	0.64	1.98	0.0040	0.178	0.092	0.270
30	3.11	8.74	0.64	2.06	0.0037	0.175	0.085	9.260
40	3.34	8.69	0.95	1.91	0.0039	0.166	0.090	0.256
60	4.00	8.73	1.66	1.93	0.0038	0.166	0.088	0.253
80	5.00	8.84	2.62	2.14	0.0033	0.166	0.076	0.242

TABLE VII

As, 19.90; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *t*, 10

n	*h*	$As-x'$	*ic*	$r=\frac{h-ic}{x'}$	*k'*	*Rip*	*Ra*	*Rip* + *Ra*
0	—	—	—	—	—	0.000	0.536	0.536
4	2.85	17.63	0.04	1.24	0.0053	0.296	0.243	0.539
6	3.05	17.79	0.06	1.41	0.0049	0.314	0.224	0.538
8	3.10	17.77	0.08	1.41	0.0049	0.317	0.227	0.544
10	3.20	17.83	0.10	1.50	0.0048	0.325	0.220	0.545
12	3.30	18.03	0.14	1.51	0.0043	0.330	0.198	0.534
15	3.44	18.07	0.19	1.77	0.0042	0.340	0.194	0.534
20	3.57	18.12	0.26	1.86	0.0041	0.346	0.188	0.534
30	3.76	18.26	0.43	2.05	0.0037	0.347	0.172	0.519
50	4.40	18.27	0.95	2.12	0.0037	0.359	0.172	0.531
70	4.80	18.31	1.45	2.11	0.0036	0.348	0.167	0.515

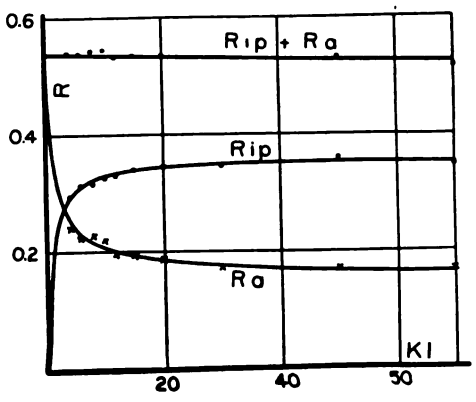

TABLE VIII

As, 9.94; *KI*, *n*.9.8; *Cr*, 40; *Ac*, 242; *t*, 10

n	*h*	$As - x'$	*ic*	$r = \frac{h - ic}{x'}$	*k'*	*Rip*	*Ra*	*Rip* + *Ra*
0	—	—	—	—	—	0.000	0.500	0.500
5	2.87	8.12	0.09	1.53	0.0088	0.303	0.202	0.505
10	3.10	8.28	0.18	1.76	0.0079	0.315	0.183	0.498
15	3.26	8.34	0.33	1.83	0.0076	0.316	0.176	0.492
20	3.55	8.35	0.48	1.93	0.0075	0.331	0.175	0.506
30	3.85	8.35	0.80	1.93	0.0076	0.329	0.175	0.504
50	4.82	8.40	1.80	2.00	0.0073	0.326	0.168	0.494

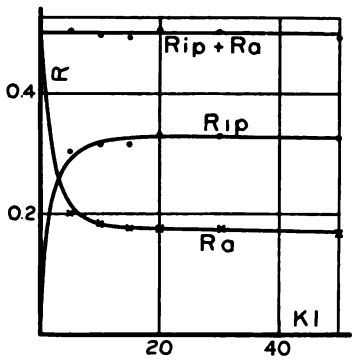

Fig. 3 (Cf. Table VIII)

TABLE IX

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 484; *t*, 10

n	*h*	$As - x'$	*ic*	$r = \frac{h - ic}{x'}$	*k'*	*Rip*	*Ra*	*Rip* + *Ra*
0	—	—	—	—	—	0.000	0.765	0.765
5	4.59	7.12	0.28	1.54	0.0183	0.487	0.306	0.793
10	5.06	7.32	0.56	1.72	0.0133	0.509	0.306	0.815
10	5.23	7.53	0.56	1.94	0.0121	0.525	0.279	0.804
15	5.54	7.58	0.84	2.00	0.0118	0.525	0.272	0.797
20	6.00	7.81	1.20	2.25	0.0105	0.531	0.242	0.773
20	5.67	7.57	1.20	1.89	0.0118	0.500	0.272	0.772
40	7.50	7.85	2.74	2.23	0.0103	0.526	0.237	0.763
40	7.44	7.50	2.74	1.93	0.0122	0.527	0.281	0.808
60	9.68	8.18	4.80	(2.83)	0.0085	0.531	0.196	0.727
60	9.13	7.77	4.80	1.83	0.0107	0.484	0.247	0.731

Note.—Thiosulphate solution 0.04 *N* was used in the measurements of this table to avoid a too great change in volume.

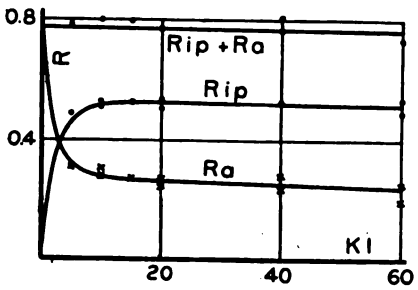

Fig. 4 (Cf. Table IX)

TABLE X

$t = 9.5$

As	10.00	20.00	10.00	10.00	10.00
KI	245	245	490	245	245
Cr	20	20	20	40	20
Ac	242	242	242	242	484
h	2.00	3.60	2.60	3.60	6.00
$As - x'$	9.15	18.30	9.18	8.50	7.70
x'	0.85	1.70	0.82	1.50	2.30
ic	0.35	0.35	0.88	0.68	1.40
$h - ic$	1.65	3.25	1.72	2.92	4.60
$r = \frac{h - ic}{x'}$	1.94	1.91	2.10	1.95	2.00
k'	0.0040	0.0040	0.0037	0.0074	0.0119
k	0.0114	0.0116	0.0114	0.0217	0.0318
$r = \frac{k - k'}{k}$	1.9	1.9	2.1	2.0	1.7

TABLE XI

As, 5.00; *KI*, 196; *Cr*, 20; *Ac*, 484

t	*h*	*ic* (*calc.*)	$h - ic$ (*calc.*)	*t*	*h*	*ic* (*calc.*)	$h - ic$ (*calc.*)
3	1.20	0.35	0.85	55	13.92	5.85	8.07
5	1.92	0.58	1.34	60	14.64	6.38	8.26
9	3.36	1.04	2.32	65	15.28	6.90	8.38
10	3.80	1.15	2.65	70	15.96	7.40	8.56
15	5.40	1.72	3.68	75	16.56	7.90	8.66
20	6.72	2.28	4.44	80	17.24	8.40	8.84
25	8.00	2.82	5.18	85	17.92	8.90	9.02
30	9.20	3.32	5.98	95	19.16	9.90	9.26
35	10.32	3.81	6.51	100	19.76	10.40	9.36
40	11.28	4.30	6.98	105	21.16	10.88	9.28
45	12.32	4.82	7.50	140	23.68	14.20	9.48
50	13.16	5.34	7.82	160	25.28	15.80	9.48

Note.—In making the iodine titrations 0.04 thiosulphate was used to avoid a too great change in volume.

Fig. 5 is plotted from the results of Table XI together with the values of x from Table XII of my paper on the oxidation of arsenious acid, and the values of x' from Table XVIII of the present paper.

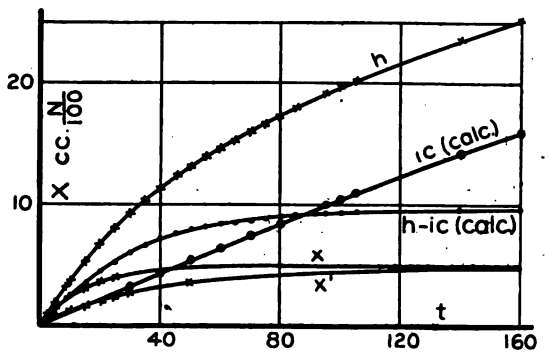

Fig. 5 (Cf. Table XI)

TABLE XII

As, 9.94; *KI*, 98; *Cr*, 20; *Ac*, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
10	1.74	9.00	0.94	0.10	1.64	1.75	0.0043
10	1.93	9.16	0.78	0.10	1.88	(2.41)	(0.0036)
15	2.52	8.56	1.38	0.15	2.37	1.72	0.0043
20	3.40	8.23	1.71	0.20	3.20	1.87	0.0041
30	4.75	7.52	2.42	0.30	4.45	1.84	0.0040
						Avg. 1.80	*Avg.* 0.0041

TABLE XIII

As, 9.94; *KI*, 196; *Cr*, 20; *Ac*, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	0.98	9.48	0.46	0.14	0.84	1.83	0.0041
10	1.88	9.00	0.94	0.27	1.61	1.71	0.0043
15	2.78	8.63	1.31	0.40	2.38	1.83	0.0041
15	2.74	8.55	1.39	0.40	2.34	1.69	0.0044
20	3.66	8.23	1.71	0.54	3.12	1.82	0.0041
25	4.40	7.84	2.10	0.67	3.73	1.78	0.0041
30	5.14	7.58	2.36	0.81	4.33	1.84	0.0039
						Avg. 1.80	*Avg.* 0.0041

TABLE XIV

As, 9.94; *KI*, 294; *Cr*, 20; *Ac*, 242

t	h	$As-x'$	ic	$r=\frac{h-ic}{x'}$	k'	x	$x\,(calc.)$	$h-ic+x'$
10	2.00	9.18	0.43	2.07	0.0035	—	--	—
10	2.17	9.12	0.43	2.12	0.0037	2.34	2.56	2.56
15	3.15	8.67	0.64	1.98	0.0040	3.28	3.75	3.78
15	3.11	8.74	0.64	2.08	0.0037	3.28	3.75	3.67
20	4.00	8.42	0.85	2.07	0.0036	3.99	4.76	4.67
30	5.67	7.74	1.28	2.00	0.0036	5.35	6.68	6.59
40	7.26	7.12	1.70	1.97	0.0038	6.50	8.86	8.38

Note.—The values of x of this table are taken from Table VIII of the paper on the oxidation of arsenious acid; $x(calc.)$ is calculated as described in the foot-note on page 73.

TABLE XV

As, 5.00; *KI*, 196; *Cr*, 20; *Ac*, 242,

t	h	$As-x'$	x'	ic	$h-ic$	$r=\frac{h-ic}{x'}$	k'
10	1.15	4.57	0.43	0.27	0.88	2.05	0.0039
15	1.62	4.40	0.60	0.40	1.22	2.03	0.0037
20	2.10	4.19	0.81	0.54	1.56	1.93	0.0038
25	2.58	4.04	0.96	0.67	1.91	1.99	0.0037
30	3.04	3.85	1.15	0.81	2.23	1.94	0.0038
						Avg. 1.99	*Avg.* 0.0038

TABLE XVI

As, 5.00; *KI*, 196; *Cr*, 40; *Ac*, 242

t	h	$As-x'$	x'	ic	$h-ic$	$r=\frac{h-ic}{x'}$	k'
5	1.10	4.69	0.31	0.24	0.86	(2.77)	(0.0056)
10	2.02	4.24	0.76	0.48	1.54	2.03	0.0072
15	2.83	3.85	1.15	0.72	2.11	1.94	0.0076
20	3.63	3.58	1.42	0.96	2.67	1.88	0.0073
30	5.09	3.05	1.95	1.44	3.65	1.87	0.0072
						Avg. 1.93	*Avg.* 0.0073

TABLE XVII

As, 9.94; *KI*, 196; *Cr*, 40; *Ac*, 242

t	h	$As-x'$	x'	ic	$h-ic$	$r=\frac{h-ic}{x'}$	k'
5	1.84	9.14	0.80	0.25	1.59	1.99	0.0073
10	3.46	8.44	1.50	0.50	2.96	1.97	0.0071
15	4.87	7.79	2.15	0.75	4.12	1.92	0.0071
						Avg. 1.95	*Avg.* 0.0072

TABLE XVIII

As, 5.00; *KI*, 196; *Cr*, 20; *Ac*, 484

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	1.90	4.30	0.70	0.60	1.30	1.86	(0.0131)
10	3.59	3.80	1.20	1.20	2.39	1.99	0.0119
15	5.16	3.37	1.63	1.80	3.36	2.06	0.0114
20	6.48	2.95	2.05	2.40	4.08	1.99	0.0115
						Avg. 1.98	*Avg.* 0.0116

TABLE XIX

As, 9.94; *KI*, 196; *Cr*, 20; *Ac*, 484

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	3.05	8.61	1.33	0.60	2.45	1.84	(0.0125)
10	5.67	7.57	2.37	1.20	4.47	1.89	0.0118
15	8.03	6.64	3.30	1.80	6.25	1.89	0.0117
						Avg. 1.87	*Avg.* 0.0118

TABLE XX

As, 9.94; *KI*, 196; *Cr*, 20; *Ac*, 242 (*Temperature 10° C*)

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
10	2.55	8.90	1.04	0.35	2.20	2.1	0.0048
15	3.53	8.26	1.68	0.52	3.01	1.8	0.0054
20	4.56	7.84	2.10	0.70	3.86	1.8	0.0052
25	5.55	7.33	2.61	0.87	4.68	1.8	0.0055
						Avg. 1.9	*Avg.* 0.0054

TABLE XXI

KI, 98; *Cr*, 20;

Ac, 242		*KI*, 196; *Cr*, 20; *Ac*, 242				*KI*, 294; *Cr*, 20; *Ac*, 242.			
ic	t	ic 0° C	t 0° C	ic 10° C	t 10° C	ic	t	ic	t
0.20	11	0.25	9.2	0.30	10	0.48	11	2.00	46
0.28	30	0.50	18.7	0.50	15	0.81	19	2.40	57
0.83	86	1.10	42	0.85	25	1.40	31	3.20	75
1.23	120	1.20	45.5	1.10	30	1.48	35	3.84	90

KI, 392; *Cr*, 20; *Ac*, 242. *KI*, 245; *Cr*, 20; *Ac*, 242. *KI*, 686; *Cr*, 20; *Ac*, 242

ic	*t*	*ic*	*t*	*ic*	*t*	*ic*	*t*	*ic*	*t*	*ic*	*t*
0.24	4.2	0.87	14.5	0.31	9.5	1.33	38	0.40	2.5	2.00	13.5
0.30	5.0	1.00	17.0	0.50	14.0	1.68	47.5	0.80	5.5	3.55	26
0.58	10.0	1.21	20.2	0.67	19.0	2.00	57	1.10	7.5	3.75	27
0.80	13.2	1.20	20.7	1.02	28.5	2.64	76	1.45	10	4.10	30.4

KI, 196; *Cr*, 40; *Ac*, 242. *KI*, 196; *Cr*, 20; *Ac*, 484. *KI*, 490; *Cr*, 10; *Ac*, 242

ic	*t*	*ic*	*t*	*ic*	*t*
0.27	5	0.60	5	0.29	6
0.44	7.5	1.20	10	0.52	13
0.57	10	1.82	15	0.66	17
0.78	15	2.43	20	0.76	19.5
1.03	20	3.00	25	0.95	25.5
1.75	35	3.60	31	1.19	32
1.98	40	4.20	35	1.42	40
2.40	50	—	—	—	—

Table XXII

Table XII r'	Table XIII r'	Table XIV r'	Table XV r'	Table XVI r'	Table XVII r'	Table XVIII r'	Table XIX r'
1.7	1.7	1.5	(2.6)	(2.8)	1.7	1.4	2.4
(2.5)	1.6	2.0	1.7	2.0	1.4	2.3	1.4
1.5	1.5	1.7	1.5	1.5	—	1.5	—
1.6	1.5	1.7	—	—	—	—	—
—	1.5	1.5	—	—	—	—	—
r''	r''	r''	r''	r''	r''	r''	r''
1.9	1.9	1.9	(2.5)	(2.7)	1.9	(3.5)	2.3
2.1	1.8	2.1	1.9	2.2	1.8	(3.0)	2.1
1.8	1.8	2.1	2.0	2.1	1.6	2.4	1.9
1.9	1.8	2.0	1.8	1.9	—	2.3	—
1.7	1.8	1.9	1.7	1.8	—	—	—
—	1.7	1.8	—	—	—	—	—
—	1 6	1.6	—	—	—	—	—

TABLE XXIII

Table	IV	V	VI	VII	VII	IX
As	10	10	10	20	10	10
KI	300+	150+	150+	300+	150+	150+
Cr	20	20	20	20	40	20
Ac	121	242	242	242	242	484
k	0.0044	0.0114	0.0114	0.0116	0.0217	0.0318
k'	0.0013	0.0037	0.0038	0.0037	0.0076	0.0112
$r+1=\frac{k}{k'}$	3.4	3.1	3.0	3.1	2.9	2.9
$r=\frac{k-k'}{k'}$	2.4	2.1	2.0	2.1	1.9	1.9

Table	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
As	10	10	10	5	5	10	5	10
KI	98	196	294	196	196	196	196	196
Cr	20	20	20	20	40	40	20	20
Ac	242	242	242	242	242	242	484	484
k	0.0114	0.0114	0.0114	0.0114	0.0200	0.0217	0.0300	0.0318
k'	0.0041	0.0041	0.0037	0.0038	0.0073	0.0072	0.0116	0.0118
$r+1=\frac{k}{k'}$	2.8	2.8	3.1	3.0	3.0	3.0	2.6	2.7
$r=\frac{k-k'}{k'}$	1.8	1.8	2.1	2.0	2.0	2.0	1.6	1.7

Note.—See also Table X.

Discussion of the Experimental Data

The measurements recorded above together with those of my previous papers on the action of chromic acid on iodide[1] and arsenious acid[2] constitute all the experimental data on which the theory developed in the following pages is based. In order to collect all the facts together the generalizations deduced in the last-mentioned papers are quoted in the following paragraphs along with the general conclusions drawn from the tables of the present paper.

Effect of the Concentration of the Iodide

Tables IV–IX (in each of which *t* is constant) show that increasing the concentration of the iodide causes a gradual

[1] See equation (1).

[2] See equation (2).

increase in the value of $h - ic$ (the iodine liberated due to the presence of the arsenious acid), and a gradual decrease in the value of x' (the arsenious acid oxidized in the presence of iodide), a maximum value of $h - ic$ and a minimum value of x' being reached when the concentration of the iodide is about fifteen times that of the arsenious acid, that is, when $KI = 15As$. Further increase in the concentration of the iodide does not appreciably affect these limiting values of $h - ic$ and x'.

When the iodide is in excess the value of the ratio, $\frac{h - ic}{x'}$, is 2.00 within the limit of the experimental error, no matter what the concentrations of the other reagents are. Thus in Tables XII–XX the average values of this ratio are, 1.80, 1.80, 2.04, 1.99, 1.93, 1.95, 1.98, 1.87 and 1.9 (at 10° C); in Table IV the values are, 2.06, 2.25, 2.07, 2.18, 2.04 and 1.94; and in Table X, 1.94, 1.91, 2.10, 1.95 and 2.00. Additional evidence is afforded by the measurements of Tables V–IX (Figs. 1–4) and the curves of Fig. 5.[1] The slight deviations in both directions, from the number 2.00 must be ascribed to experimental error, for the ratio in question is the quotient of two small numbers, each of which is the difference between two small readings of the burette, and owing to the nature of the method of analysis it usually happens that when one of these numbers (say $h - ic$) is too small the other (x') is too large.

Tables V–IX and the curves of Figs. 1–4, show that addition of potassium iodide lessens the rate of oxidation of arsenious acid by chromic acid, the retardation increasing with the concentration of the iodide up to a certain point from which on (Ra, when $KI = 0$, being equal to Rac),

$$Ra, (KI\ excess) = \frac{I}{3} \cdot Rac. \qquad (7)$$

Additional evidence of relation (7) is afforded by Table XXIII in which k is seen to closely equal 3 k'.

[1] The curve, $h - ic$, approaches the line, $N = 10 = 2As$, asymptotically, and simultaneously the curve, x', approaches the line, $N = 5 = As$.

Tables V–IX and Figs. 1–4 further show that the rate at which iodine is liberated in solutions containing arsenious and chromic acids, after correcting for the direct oxidation of iodide by chromic acid, increases with the concentration of the iodide up to a certain point from which on,

$$Rip,\ (KI\ excess) = 2Ra,\ (KI\ excess) \qquad (8)$$
$$= \frac{2}{3} \cdot Rac.$$

The last columns of Tables V–IX and the upper curves of Figs. 1–4, show that the sum, $Ra + Rip$, that is, the rate of reduction of chromic acid[1] after correcting for the direct action of the chromic acid on the iodide, is the same for all concentrations of iodide from zero up, or,

$$Ra + Ri - Ric = Rac \qquad (9)$$

that is,

$$Ra + Rip = Rac. \qquad (10)$$

Thus M of equation (5) is $-Rip$.

In the absence of arsenious acid the rate of oxidation of iodide by chromic acid is connected with the concentration of the iodide by a quadratic relation (see equation 1).

---

[1] On comparing the above Tables of results with those on the oxidation of arsenious acid in the absence of iodide, it will be noticed, however, that for any fixed interval of time the total oxidation is greater in the presence than in the absence of the iodide, that is, $h - ic + x'$ is greater than x for a fixed time. This is due to the fact that in the former case the concentration of the arsenious acid (on which the $h - ic$ reading depends) does not fall off so rapidly as in the latter case. If the average concentration of the arsenious acid had remained the same as it did in the experiments in which iodide was present, we would have for the value of x:

$$x(calc) = x. \frac{As.t - \int_0^t x'.dt}{As.t - \int_0^t x.dt};$$

and as shown by Table XIV, $x(calc)$ is equal to the experimentally determined value, $h - ic + x'$. For the method of computation, see Jour. Phys. Chem., 10, 423 (1906).

Effect of the Concentration of the Arsenious Acid

In the absence of iodide the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid. This suggested computing the constant of the "first order" in the tables of the present paper. The constancy of k' in each of the Tables XII–XX, and more particularly the fact that changing the concentration of the arsenious acid in these tables as well as in Tables V, VI and VII, does not effect the value of k', shows that in the presence as well as in the absence of iodide the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid.

Since in the presence of excess of iodide, $h - ic = 2x'$ (see page 72), the rate *Rip* is twice the rate *Ra*, (*KIexcess*), and is therefore, like the latter, proportional to the concentration of the arsenious acid. The fact that $Rip + Ra = Rac$ for all concentrations of iodide from zero up, is also proof that *Rip* is proportional to the first power of the concentration of the arsenious acid.

Effect of the Concentration of the Bichromate

Comparison of Tables V and VIII, XV and XVI, XIII and XVII, shows that doubling the concentration of the bichromate almost doubles the value of k', that is, almost doubles the rate of oxidation of arsenious acid, *Ra*, when iodide is present; or the rate *Ra* is proportional to about the o.9*th* power of the concentration of the bichromate.

In the absence of iodide the same relation was found to hold; that is, *Rac* is proportional to the o.9*th* power of the concentration of the bichromate.

Since in the presence of excess of iodide $h - ic = 2x'$, the rate *Rip* is twice the rate *Ra*, (*KI excess*), and is therefore like the latter proportional to the same (o.9*th*) power of the concentration of the bichromate; and the fact that $Rip + Ra = Rac$ is also proof that the rate *Rip* is proportional to the o.9*th* power of the concentration of the bichromate.

In the absence of arsenious acid the rate of oxidation of

iodide (*Ric*) was found to be proportional to a power of the bichromate slightly less than the first (except when very dilute solutions of bichromate were employed, when the power was the first exactly). In the above tables *ic* is scarcely doubled for a fixed interval by doubling the concentration of the bichromate.

Thus the rates *Rac Ra*, *Rip* and *Ric* are each proportional to a power of the concentration of the bichromate slightly less than the first.

Effect of the Concentration of the Sulphuric Acid

Doubling the concentration of the sulphuric acid nearly trebles the rates *Ra* and *Rip* in Tables V and IX, and the constants k' in Tables XV and XVIII, XIII and XIX. Thus the rates *Ra* and *Rip* are proportional to the 1.4*th* power of the concentration of the sulphuric acid.

The rate of oxidation of arsenious acid in the absence of iodide is also proportional to the 1.4*th* power of the concentration of the sulphuric acid. This unusual fractional power is thus common to the kinetic formulae for the rates *Rac*, *Ra* and *Rip*, while the rate of oxidation of iodide in the absence of arsenious acid (*Ric*) is proportional to the square of the concentration of the sulphuric acid.

Effect of the Temperature

Changing the temperature from 0° *C* to 10° *C* causes a change in the constant k' of 29 *percent* (0.0041 to 0.0053, Tables XIII and XX). Since in these tables $h - ic = 2x'$, the rate *Rip* is also increased by the same amount.

Changing the temperature has practically the same effect on the rate of oxidation of arsenious acid in the absence of iodide (*Rac*); the experiments showed that changing the temperature from 0° *C* to 10° *C* causes a change of 26 *percent* in the constant k (0.0114 to 0.0144).

Thus the rates *Rac*, *Ra* and *Rip* have the same unusually low temperature coefficient, *viz.*, less than 1.3.

The temperature coefficient of the rate of oxidation of iodide by chromic acid is also very low, *viz.*, 1.4.

Short Statement of the Results

The following are the general results of the experiments:

$$Rac = k.As\ (Cr)^{0.9}.(Ac)^{1.4} \qquad (11)$$

$$Ra = k'.As\ (Cr)^{0.9}.(Ac)^{1.4} \qquad (12)$$

$$Ric = K.(m.KI + n.(KI)^2).Cr.(Ac)^2, \qquad \text{Compare equation (1)}$$

$$Ri - Ric = Rip = k''.As.(Cr)^{0.9}.(Ac)^{1.4} \qquad (13)$$

and $$Rac = Ra + Rip.$$

The constants k' and k'' depend on the amount of iodide present: as the concentration of the iodide increases, k' decreases from k, for $KI = 0$, to $\frac{k}{3}$, for *KI, excess*; and simultaneously k'' increases from 0 to $2k'$ or $2\frac{k}{3}$.

When the iodide is in excess the ratio $\frac{h - ic}{x'}$ is equal to 2.

The rates *Rac*, *Ra*, (*KI excess*) and *Rip*, (*KI excess*) have the same unusually low temperature coefficient, *viz.*, less than 1.3 (from 0° *C* to 10° *C*); the temperature coefficient for the rate *Ric* is about 1.4.

THEORETICAL PART

The above results show that:

(*a*) The rate of reduction of chromic acid in solutions containing arsenious acid and iodide is equal to the sum of the rates of reduction of chromic acid by arsenious acid and by iodide taken separately, or, in other words, the acceleration of the rate of oxidation of iodide is just equal to the retardation in the rate of oxidation of arsenious acid.

(*b*) The effects of temperature and the concentrations of the various reagents are the same for the three rates:

(*i*) Oxidation of arsenious acid by chromic acid in the absence of iodide (*Rac*).

(*ii*) Oxidation of arsenious acid by chromic acid in the presence of excess of iodide (*Ra, KI excess*).

(*iii*) Oxidation of iodide in the presence of arsenious acid, when the iodide is in excess (*Rip, KI excess*).

(*c*) The ratio $Ra:Rip$ is independent of the concentrations of the bichromate and sulphuric acid for all concentrations of iodide.

(*d*) In the absence of arsenious acid the rate of oxidation of iodide is proportional to powers of the concentrations of the reagents somewhat different from those of rates (*i*), (*ii*) and (*iii*) of (*b*).

These facts suggest the theory of the formation of a primary oxide when chromic acid acts on arsenious acid, and the succeeding paragraphs will show that the above experimental results may be satisfactorily accounted for by the following assumptions.

Assumptions

(*a*) That arsenious acid acting on chromic acid forms slowly a primary oxide.

(*b*) That this oxide is completely and instantaneously reduced by either arsenious acid or iodide.

(*c*) That the fractions of the primary oxide reduced by arsenious acid and iodide respectively, in solutions containing both, depend on their relative concentrations; when the iodide is in large excess the amount of the primary oxide reduced by the arsenious acid is negligible.

The primary oxide may be one of the following:[1]

(1) *A peroxide of arsenic represented by the formula,* As_2O_9, *or one of its hydrates, e. g.,* H_3AsO_6, the reactions being as follows:

(*i*) Slow formation of the peroxide,

$$As_2O_3 + 2K_2Cr_2O_7 + 3H_2SO_4 = As_2O_9 + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 3H_2O;$$

or,

$$\overline{\overline{\overline{AsO_3}}} + \overline{\overline{Cr_2O_7}} + 2\overset{+}{H} = \overline{\overline{\overline{AsO_6}}} + Cr_2O_3 + H_2O. \qquad (14)$$

(*ii*) Rapid reduction by arsenious acid or iodide,

$$As_2O_3 + 2As_2O_3 = 3As_2O_5; \text{ or, } \overline{\overline{\overline{AsO_6}}} + 2\overline{\overline{\overline{AsO_3}}} = 3\overline{\overline{\overline{AsO_4}}} \qquad (15)$$

and

[1] For methods of determining the degree of oxidation of the primary oxide, see p. 83.

$As_2O_9 + 8HI = As_2O_5 + 4I_2 + 4H_2O$; or,

$$\overline{\overline{\overline{As}}}O_6 + 4\bar{I} + 4\overset{+}{H} = \overline{\overline{\overline{As}}}O_4 + 2I_2 + 2H_2O. \quad (16)$$

(2) *An intermediate oxide*[1] *of chromium of the formula* Cr_2O_5, *or one of its hydrates, e. g.,* $H_2Cr_2O_6$, the reactions being as follows:

(*i*) Slow formation of the intermediate oxide (peroxide),

$As_2O_3 + 2K_2Cr_2O_7 = As_2O_5 + 2K_2Cr_2O_6$; *i. e.*,

$$As_2O_3 + 4CrO_3 = As_2O_5 + 2Cr_2O_5;$$

or,

$$\overline{\overline{\overline{As}}}O_3 + \overline{\overline{Cr}}_2O_7 = \overline{\overline{\overline{As}}}O_4 + \overline{\overline{Cr}}_2O_6. \quad (14a)$$

(*ii*) Rapid reduction by arsenious acid or iodide,

$Cr_2O_5 + As_2O_3 = Cr_2O_3 + As_2O_5$; or,

$$\overline{\overline{Cr}}_2O_6 + 2\overline{\overline{\overline{As}}}O_3 = \overline{\overline{Cr}}_2O_4 + 2\overline{\overline{\overline{As}}}O_4 \quad (15a)$$

and

$Cr_2O_5 + 4HI = Cr_2O_3 + 2I_2 + 2H_2O$; or,

$$\overline{\overline{Cr}}_2O_6 + 4\bar{I} + 4\overset{+}{H} = \overline{\overline{Cr}}_2O_4 + 2I_2 + 2H_2O \quad (16a)$$

(3) *A mixed peroxide of arsenic and chromium of the same degree of oxidation as* (1) *and* (2).

Development of the Theory

It has been found convenient to introduce the symbol *Rp*, for the rate of formation of the hypothetical oxide, according to equations (14) or (14*a*), the unit being 0.25×10^{-5} formula-weights if the oxide As_2O_9 be assumed, or 0.5×10^{-5} formula-weights if the oxide Cr_2O_5 be assumed, and the symbol *Rap* for the rate of oxidation of arsenious acid by peroxide, according to equations (15) and (15*a*). *Rip* has already been introduced (page 57): it may now be defined as the rate of oxidation of iodide by peroxide, as in equations (16) and (16*a*).

If the solution contains chromic and arsenious acids only, then for every unit of arsenious acid oxidized in the first stage

[1] Although the formula Cr_2O_5 contains less oxygen than the formula CrO_3 I shall speak of it as a peroxide of chromium.

(formation of peroxide, equations (14) and (14*a*)) two more are oxidized in the second stage (reduction of peroxide, equations (15) and (15*a*)), the final result being the formation of three units of arsenic acid. As, by hypothesis, the second stage takes place instantaneously, the time required for the formation of this amount of arsenic acid is practically that involved in the formation of a unit of peroxide, or,

$$Rp = \frac{1}{3} \cdot Rac. \qquad (17)$$

If, however, the solution contains iodide as well as arsenious acid, both will be oxidized on the reduction of the peroxide, the total quantity of iodine and arsenic acid formed in the second stage amounting to two units in all. As before, for one unit of peroxide formed and reduced three units of arsenic acid and iodine taken together are generated, and

$$Rp = \frac{1}{3}(Ra + Rip). \qquad (18)$$

Whether iodide be present or not, however, for every unit of peroxide formed one unit of arsenious acid must be oxidized to arsenic acid;[1] any additional arsenic acid formed is due to the oxidation of arsenious acid by the peroxide. Thus,

$$Ra = Rp + Rap \qquad (19)$$

It has been pointed out in the paragraph preceding equation (18), that two units of iodine and arsenic acid counted together are formed by the reduction of one unit of peroxide; the share of these two units, however, that falls to each, depends upon the relative concentrations of the iodide and arsenious acid. As the concentration of the iodide is increased, the reaction represented by equation (15) or (15*a*), falls more and more into the background until in the presence of large excess of iodide,

$$Rap, (KI\ excess) = 0 \qquad (20)$$

[1] If the peroxide be Cr_2O_5, this unit of arsenic acid is formed in the first stage, equation (14*a*); if As_2O_5, from the peroxide on reduction, equations (15) and (16).

whence by equation (19),

$$Ra,\ (KI\ excess) = Rp \qquad (21)$$

and by equation (18),

$$Rip,\ (KI\ excess) = 2\,Rp. \qquad (22)$$

Comparison of the Theory with Results of the Experiments

By eliminating the hypothetical Rp from equations (17) to (22) the relations deduced from the assumptions of page 77, may be compared with the experimental results.

The elimination gives:

From equations (17) and (18),

$$Ra + Rip = Rac,$$

which is the same as equation (10); from equations (17) and (21),

$$Ra,(KI\ excess) = \frac{1}{3} \cdot Rac,$$

which is the same as equation (7); also from equations (21) and (22),

$$Rip,\ (KI\ excess) = 2Ra,\ (KI\ excess) = \frac{2}{3} \cdot Rac$$

which is the same as equation (8).

That is to say, the main quantitative relations between the rates of oxidation of acceptor and inductor are in accordance with the postulates of the theory set forth on page 77. These relations are clearly shown in Fig. 6, which is in obvious agreement with Figs. 1 to 5, where the curves were plotted from the experimental data.

Further Development of the Theory

A graphic representation of the theoretical relations is given in Fig. 6, where the dotted line shows the general form of the Rip curve for increasing concentration of iodide.

Conclusions as to the relative *effects of the reagents on the rates, Rap and Rip* might be drawn from the form of the *Rap*

and *Rip* curves before they become horizontal; unfortunately, the experimental errors incident to the method of analysis are greatest when the concentration of the iodide is small and this renders any detailed study of the curves useless.

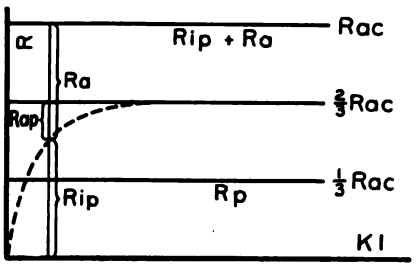

Fig. 6

However, from Tables V and VI it appears that in solutions containing *As* 10, *Cr* 20, *Ac* 242, the rates *Rip* and *Rap* are equal when *KI* is about 25. If *Rip* were proportional to the first power of the concentration of the iodide then for $KI = 150$, $\frac{Rip}{Rap}$ would be 6; and if to the second power of the iodide, 36. The first is certainly far too low to be in agreement with the results while the second is not.

Again, comparison of Tables VI and VII shows that when the concentrations of both the arsenic and iodide are doubled the ratio $\frac{Rip}{Rap}$ is increased; or in other words the arsenious acid has less effect on the rate *Rap* than the iodide has on the rate *Rip*; if *Rip* be set proportional to the second power of the concentration of the iodide (in accordance with the conclusion reached in last paragraph), then *Rap* must be set proportional to some lower power of the concentration of the arsenious acid—perhaps the first.

Nature of the Primary Oxide

As has been shown on page 77 the experimental results of the present paper accord equally well with either of the following assumptions:

(1) A peroxide of arsenic.

(2) A peroxide of chromium.

(3) A complex peroxide of chromium and arsenic.

If one is to choose between these assumptions, additional evidence is necessary. Such evidence may possibly be obtained in the following ways:

(*a*) *By comparison of the powers of the reagents corresponding to the various hypotheses, with those obtained by experiment*—as suggested by Van't Hoff.

Equations (14) and (14*a*), corresponding to the assumptions of a peroxide of arsenic and one of chromium respectively both agree with the fact that the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid and to the 0.9*th* power of the concentration of the bichromate (regarding the chromic acid as not being completely dissociated); and equation (14), together with the view that an ion[1] of arsenious acid reacts with chromic acid, satisfactorily accounts for the effect of the sulphuric acid concentration, while equation (14*a*) offers no explanation of the effect of the concentration of the acid. We thus have an argument in favor of assumption (1) or (3), and against assumption (2).

(*b*) *By "systematic variation of the three reagents,"* as suggested by Luther and Schilow.[2]

Many qualitative experiments were made substituting for chromic acid other oxidizing agents, such as, H_2O_2, $K_2S_2O_8$, $KBrO_3$, $KClO_3$, $KClO_4$, using starch as indicator for the iodine liberated, and keeping the concentrations of the iodide and sulphuric acid sufficiently large to prevent the arsenious acid from acting on the liberated iodine. In no case was the oxidation of iodide found to be accelerated by the addition of arsenious acid. Thus we have evidence that the primary oxide is a compound of chromium (assumptions (2) and (3)).

Also when certain reducing agents are substituted for

[1] See the paper on the rate of oxidation of arsenious acid by chromic acid.

[2] Zeit. phys. Chem. **46**, 816 (1903).

arsenious acid the rate of oxidation of iodide by chromic acid is accelerated; this is noticeable in the case of some organic acids as tartaric and oxalic acids[1] and in the case of ferrous salts[2] in this last case, however, the acceleration cannot be ascribed to the formation of a peroxide, as Miss Benson has shown. So too, in any given case, to account for the acceleration, different types of intermediate compounds may be assumed in the absence of definite knowledge of the kinetics of the reactions, and it is in this particular that the method suggested by Luther and Schilow fails.

Summing up the evidence brought forward by the application of the above two methods, (*a*) and (*b*), we find arguments for and against the assumptions that the primary oxide is one of arsenic or one of chromium, (1) and (2), but none contrary to the view that the primary product is a complex peroxide of arsenic and chromium (3).

Determination of the Degree of Oxidation of a Hypothetical Primary Oxide

The problem of determining the degree of oxidation of an assumed primary oxide is of general interest, and some methods of doing so will now be given, using the present case in illustration.

(*a*) *From the ratio of the quantities of acceptor and inductor oxidized in any interval* (*induction factor*), *when the concentration of the acceptor is so great that this ratio has become constant* (as employed by Manchot, Luther and Schilow and others).

Let the composition of the peroxide be represented by the general formula, As_2O_{5+2r}. Then the reaction between the peroxide and arsenious acid must be written:

$$As_2O_{5+2r} + rAs_2O_3 = (r+1)As_2O_5 \qquad (23)$$

and that between the peroxide and the iodide,

$$As_2O_{5+2r} + 4rHI = 2rI_2 + As_2O_3 + 2rH_2O. \qquad (24)$$

[1] I have made some measurements on this subject, and these I hope soon to complete and publish.

[2] Manchot: loc. cit.; Miss C. C. Benson: loc. cit.

When the iodide is in excess reaction (23) is negligible, and hence for every equivalent of arsenic acid formed r equivalents of iodine are liberated, or,

$$\frac{h-ic}{x'}(KI\ excess) = r, \qquad (25)$$

where $h-ic$ and x' are the amounts of iodide and of arsenious acid oxidized in the same time (both quantities being expressed in *cc* of 0.01 *N* solution) see page 61.

As shown on page 72, $r=2$, and hence the peroxide is As_2O_9.

If a primary oxide of chromium be assumed the treatment is similar. Regarding CrO_3 and Cr_2O_3 as the initial and final oxides in the reduction of chromic acid, let the general formula of the peroxide be Cr_2O_{3+s}. Then for the formation of this oxide we have:

$$2CrO_3 + \frac{3-s}{2}As_2O_3 = Cr_2O_{3+s} + \frac{3-s}{2}As_2O_5; \qquad (26)$$

for the oxidation of arsenious acid by peroxide,

$$Cr_2O_{3+s} + \frac{s}{2}As_2O_3 = Cr_2O_3 + \frac{s}{2}As_2O_5; \qquad (27)$$

and for the reaction between peroxide and iodide,

$$Cr_2O_{3+s} + 2sHI = Cr_2O_3 + sI_2. \qquad (28)$$

When the iodide is in excess, reaction (27) is negligible, hence,

$$\frac{h-ic}{x'}(KI\ excess) = \frac{s}{3-s}. \qquad (29)$$

As shown on page 72 the value of the ratio $(h-ic):x'$, when the iodide is in excess, is 2, hence $s=2$, and the formula of the peroxide is Cr_2O_5.

(*b*) *From the ratio of the rates of oxidation of the inductor in the absence of the acceptor to that in the presence of excess of the acceptor.*

If the peroxide be one of arsenic, As_2O_{5+2r}, we have from equations (23) and (24):

$$\frac{Rac}{Ra,(KI\ excess)} = r+1, \text{ or, } \frac{Rac-Ra,(KI\ excess)}{Ra,(KI\ excess)} = r. \qquad (30)$$

Hence from the definitions of k and k' given on page 62.

$$\frac{k}{k'} = r + 1, \text{ or, } \frac{k-k'}{k'} = r. \qquad (31)$$

Or if a peroxide of chromium, Cr_2O_{3+s}, be assumed, we have from equations (26) and (27):

$$\frac{Rac}{Ra, (KI\ excess)} = \frac{3}{3-s} \text{ or, } \frac{Rac-Ra, (KI\ excess)}{Ra, (KI\ excess)} = \frac{s}{3-s} \qquad (32)$$

hence also,

$$\frac{k}{k'} = \frac{3}{3-s}, \text{ or, } \frac{k-k'}{k'} = \frac{s}{3-s}. \qquad (33)$$

In Tables V–IX it is seen that the value of the ratio $Rac : Ra$, $(KI\ excess)$ is very close to 3: hence from equation (30), $r=2$, and from equation (32), $s=2$. In the summary, Table XXIII, the value of the ratio, $k:k'$ is seen to be 3; hence again r and s have the value 2 (equations (31) and (33)). Thus the formula of the peroxide must be written, As_2O_9 or Cr_2O_5.

(*c*) *From the amounts of the acceptor oxidized in known intervals, assuming that the law of the oxidation of the inductor in the absence of acceptor is known.*

It is generally very difficult to determine the amounts of each of two reducing agents in the presence of an oxidizing agent, and quite often impossible to find accurately the induction factor (when the reaction is over); in such cases if it is possible to make near the beginning of the reaction a few measurements of the amount of acceptor oxidized when this reagent is in excess, the degree of oxidation of the primary product may be calculated by the following methods.

The rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid; thus using the symbols defined on page 62, we have,

$$k = \frac{1}{t} . log_{10} \frac{As}{As-x} \qquad (34)$$

and when the acceptor is present in excess,

$$k' = \frac{1}{t} . log_{10} \frac{As}{As-x'}. \qquad (35)$$

When the acceptor is in excess, we have, assuming the formula of the peroxide to be As_2O_{5+2r}

$$\frac{h-ic}{x'}(KI\ excess) = r$$

whence, writing a for $h - ic$ to economize space,

$$x' = \frac{a}{r}$$

and we have,

$$\frac{1}{t_1}.\log_{10}\frac{As}{As-\frac{a_1}{r}} = \frac{1}{t_2}.\log_{10}\frac{As}{As-\frac{a_2}{r}} = \frac{1}{t_3}.\log_{10}\frac{As}{As-\frac{a_3}{r}} = \ldots \qquad (36)$$

where t_1, a_1; t_2, a_2; t_3, a_3; etc., are experimentally determined values of t and a.

(*i*) This equation may be solved for r, most simply by testing in turn, the numbers, 1, 2, etc.

If the rate of oxidation of the inductor had been proportional to any other power of its concentration than the first, an equation somewhat similar to (36) could be written, to be solved for r.

(*ii*) If it be assumed that the value of k in equation (34) be known, r can be found from the following equation (which is obtained from (31) and (33)):

$$k' = \frac{k}{r+1} = \frac{1}{t}.\log_{10}\frac{As}{As-\frac{a}{r}} \qquad (37)$$

by putting it in the form,

$$\frac{2.30k}{r+1} = -\frac{1}{t}.\log_e\left(1-\frac{a}{r.As}\right)$$

$$= \frac{1}{t}\left\{\frac{a}{r.As} + \frac{1}{2}\left(\frac{a}{r.As}\right)^2 + \frac{1}{3}\left(\frac{a}{r.As}\right)^3 + \ldots\right\}. \qquad (38)$$

If the fraction $\frac{a}{r.As}$ be very small we have as a first approximation,

$$\frac{2.30k}{r+1} = \frac{1}{t}\cdot\frac{a}{r.As} \qquad (39)$$

and since $a = h - ic$ we have,

$$r = \frac{0.4343(h-ic)}{k.t.As - 0.4343(h-ic)} = r' \text{ of Table XXII.} \qquad (40)$$

Using this approximation the values of r' given in Table XXII were calculated. It will be noticed that the value of r' diminishes as a (*i. e.*, $h - ic$) increases, because the neglected terms of equation (38) become larger and larger. Hence a closer approximation is to be desired:

$$\frac{2.30k}{r+1} = \frac{1}{t}\left(\frac{a}{r.As} + \frac{1}{t}\left(\frac{a}{r.As}\right)^2\right) \qquad (41)$$

and hence,

$$r = \frac{a}{4.As} \cdot \frac{\sqrt{(a+2.As)^2 + 8.As(2.30k.t.As - a)} + (a+2.As)}{2.30k.t.As - a} = r''$$

of Table XXII. (42)

The values of r'' in Table XXII were calculated by means of formula (42).

These values do not fall off so noticeably on increasing the value of a (*i. e.*, $h - ic$) as do the values of r' in the same table. Both r' and r'' point to the number 2 as the value of r. A slight error in k or a will cause a considerable error in the value of r''; this is noticeable in initial values of some of the tables.

(*iii*) The value of r may be found also in the following manner:

We have

$$\frac{dx'}{dt} = 2.30k'(As - x'),$$

and since $a = r.x'$, it follows that

$$\frac{da}{dt} = 2.30k'(r.As - a), \qquad (43)$$

whence,

$$a = 2.30k' \int_0^t (r.As - a).dt = 2.30k'(r.As.t - \int_0^t a.dt),$$

and therefore,

$$\frac{a}{t} = 2.30k'(r.As - \frac{1}{t}\int_0^t a.dt). \qquad (44)$$

Now the values of $\int_0^t a.dt$ can be found easily and accurately from the plotted curve, a, t, and hence the values of k' and of $r.As$ can be found by means of equation (44) for any two pairs of values of a and t.

Thus, we have

$$\frac{r.As}{As} = \frac{h-ic}{x'} \text{ (for } t = \infty) = r^1. \qquad (45)$$

If in addition the value of k of equation (34) be known, the value of r can be determined from the above calculated value of k' as in equation (31).

SUMMARY

A method of analysis, which may be of use in the study of other complicated cases of induced oxidation, is described.

Addition of potassium iodide lessens the rate of oxidation of arsenious acid by chromic acid, the retardation increasing with the concentration of the iodide up to a certain point from which on the rate of oxidation of arsenious acid is equal to one-third the rate when no iodide is present; or symbolically,

$$Ra\,(KI\ excess) = \frac{1}{3}.\,Rac.$$

The rate at which iodine is liberated in solutions containing arsenious acid, iodide and chromic acid, after correcting for the direct oxidation of iodide by chromic acid, in-

[1] As an example of this method the following table calculated from the data of Table XI, by methods described in Jour. Phys. Chem., 10, 423 (1906) is given.

	t	$\frac{1}{t}\int_0^t a.dt$	$r.As$
(1)	20	2.55	——
(2)	25	2.96	——
(3)	30	3.42	10.0, from (1) and (3)
(4)	35	3.83	10.4, from (2) and (4)
(5)	40	4.19	10.4, from (3) and (5)

In this table $a = h - ic$ (*calc.*) of Table XI. The value of As is 5.00 and hence $r = 2$ very closely.

creases with the concentration of the iodide up to a certain point from which on the rate of liberation of iodine is twice the rate of oxidation of arsenious acid (expressing both iodide and arsenious acid in equivalents), or,

$$Rip = 2Ra, \ (KI \ excess).$$

The rate of reduction of chromic acid (after correcting for the direct action of the iodide) is the same for all concentrations of iodide from zero up, or,

$$Ra + Ri - Ric = Ra + Rip = Rac.$$

Expressing each of the three rates, *Rac* (rate of oxidation of arsenious acid by chromic acid in the absence of iodide), *Ra* (rate of oxidation of arsenious acid in the presence of iodide) and *Rip* (rate of liberation of iodine after correcting for the direct action of the chromic acid on iodide), in terms of the concentrations of the reagents, we have

$$Rac = k.As.(Cr)^{0.9}.(Ac)^{1.4}$$
$$Ra = k'.As.(Cr)^{0.9}.(Ac)^{1.4}$$
$$Rip = k''.As.(Cr)^{0.9}.(Ac)^{1.4}$$

where k' and k'' depend on the concentration of the iodide. When the iodide is in excess,

$$k - 3k' = \frac{3}{2}.k''.$$

The effect of the temperature on the rates *Rac*, *Ra* (*KI excess*) and *Rip*, (*KI excess*) is the same, the coefficient being unusually small (somewhat less than 1.3).

The results may be accounted for by assuming:

(*a*) *That arsenious acid acting on chromic acid forms slowly a primary oxide.*

(*b*) *That this oxide is completely and instantaneously reduced by either arsenious acid or iodide.*

(*c*) *That the fractions of the primary oxide reduced by arsenious acid and iodide respectively, in solutions containing both, depend on their relative concentrations*: when the iodide is in large excess the amount of the primary oxide reduced by the arsenious acid is negligible.

The primary oxide may be one of the following:

(1) A peroxide of arsenic represented by the formula, As_2O_9, or one of its hydrates, *c. g.*, H_3AsO_6.

(2) An intermediate oxide of chromium of the formula, Cr_2O_5, or one of its hydrates, *c. g.*, $H_2Cr_2O_6$.

(3) A complex peroxide of arsenic and chromium of the same degree of oxidation as (1) and (2).

Other evidence is in support of the view that the peroxide is one of arsenic; and still other evidence favors the assumption that the primary oxide is a compound of chromium; *the view that the primary oxide is a complex peroxide of arsenic and chromium is, however, in best accord with all the facts.*

Methods are described by which the degree of oxidation of a hypothetical primary oxide may be determined.

The above experimental work was completed in the Chemical Laboratory of the University of Toronto in May, 1905.

I wish here to express my thanks to Professor W. Lash Miller at whose suggestion this research was undertaken, for his kind advice and assistance throughout.

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THE DETECTION AND ESTIMATION OF α-NAPHTHOQUINONE β-NAPHTHOQUINONE, PHTHALONIC ACID AND PHTHALIC ACID.

BY MAITLAND C. BOSWELL.

Received December 5th, 1906.

During the progress of a research upon the mechanism of the oxidation of naphthalene to phthalic acid, it was found necessary to be provided with methods for the detection and accurate determination of α-naphthoquinone, β-naphthoquinone, phthalonic acid and phthalic acid; and also with a method for the determination of phthalic acid in the mixture of organic acids formed by the oxidation. As no such methods are described in the chemical literature, I was forced to work them out for myself; and after a number of preliminary trials arrived at the following, which have proved very satisfactory, both as to the simplicity of the operations involved, and the accuracy of the results obtained.

Determination of α-Naphthoquinone: This compound was prepared by the method of Japp and Miller[1] which is an improvement on the method of Groves[2].

The reaction of the quinone which seemed best suited for the purposes

[1] J. Chem. Soc. 39, 220 (1881).

[2] Liebig's Ann. 167, 357, (1873).

of an analytical method is that with stannous chloride, which has been used by Plimpton[1] and by Russig[2] for the preparation of α-hydronaphthoquinone and its derivatives.

In the first experiments I treated the quinone with a large quantity of the stannous salt, and attempted to determine the excess of the latter with decinormal iodine. No satisfactory results were obtained, however, either at room temperature, or at 100°. This might be accounted for by the action of iodine on the hydro-naphthoquinone formed by the reduction; but even when the latter was removed the results were still unsatisfactory.

The plan was then changed, and the stannous salt was added to the quinone from a burette until the reduction was complete, the end point being recognized by the absence of characteristic color reactions of the quinone. Two methods of working were studied, differing in the nature of the indicator chosen; both gave good results, and in each $2SnCl_2$ were required for one mol. of $C_{10}H_6O_2$.

First Method: A decinormal solution of stannous chloride in two per cent. hydrochloric acid[3] is run into the alcoholic solution of the quinone, until the yellow color of the latter is almost discharged. The addition of the stannous chloride is then proceeded with drop by drop, testing after each addition on a watch glass, with a drop or two of a mixture of equal volumes of phenyl-hydrazine and alcohol. So long as a trace of the quinone remains a bright pink color is formed.[4] (Taken, 0.0700 g. quinone : found, 0.070 g.).

Second Method: To the alcoholic solution of the quinone, three or four drops of freshly distilled aniline are added, and the whole is boiled; whereupon it turns bright red[5]. Decinormal stannous chloride is then run in from a burette, heating to boiling after each addition, until the red color is completely discharged. If the end point has been over-stepped, a volumetric solution of the naphthoquinone may be used for titrating back. (Taken, 0.0700 g. quinone; found, 0.072 g.).

Purification of β-Naphthoquinone: This compound was prepared according to the method of Lagodzinski and Hardine[6], about 40 g. of crude quinone being obtained from 50 g. β-naphthol. No method could be found in the literature for the purification of this crude material, and attempts to recrystallize it from ether, alcohol, benzene, petroleum ether, acetone, chloroform, or mixtures of these, were unsuccessful.

[1] J. Chem. Soc. 37, 635 (1880).

[2] J. pr. Chem. 170, 32 (1900).

[3] If the acid is too concentrated, some of Knapp and Schultz's amorphous compound may be formed, Ann. 210, 178 (1881).

[4] Ber. 17, 3026, (1884).

[5] J. Chem. Soc. 37, 635 (1880).

[6] Ber. 27, 3075 (1894).

The following method based on the reduction of the quinone to the corresponding hydroquinone and subsequent oxidation of the latter, however, effects a complete purification without loss of material.

Twenty grams of the crude, dark colored quinone is placed in a 500 cc. Erlenmeyer flask, 250 cc. of water saturated with sulphur dioxide is added, the flask is corked tightly and the whole shaken violently for about half a minute or until nearly all is dissolved. The shaking must not be continued too long or there will be a loss due to the separation of hydroquinone from the solution. The mixture is then quickly filtered by suction through a Buchner perforated funnel directly into a solution containing 60 grams potassium bichromate and 40 cc. conc. sulphuric acid in 1200 cc. water cooled to 5°–10°. The suction flask should be shaken with a circular motion during the filtration. The pure quinone falls to the bottom as a bright yellow orange precipitate and a black tarry residue remains on the filter. A second portion of twenty grams crude quinone may be dissolved in sulphurous acid as before, and filtered into the same oxidizing mixture without removing the quinone already there.

Determination of β-Naphthoquinone: Decinormal stannous chloride is added from a burette to the quinone dissolved in ether. A dark green, almost black, opaque solution results; owing, probably, to the formation of a quinhydrone. On adding more tin solution a point is finally reached at which the solution in ether suddenly becomes colorless and transparent, indicating the complete reduction of the quinone to hydroquinone. Each mol. quinone requires one mol. $SnCl_2$. (Taken, 0.0700 g.; found, 0.071 g.).

Purification of Phthalonic Acid: The syrupy solution prepared from naphthalene and potassium permanganate by the method of Graebe and Trümpy[1] crystallizes on long standing in a desiccator to a solid mass, said to consist of the dihydrate of phthalonic acid[2]; I found it, however, impossible to obtain a preparation of definite composition without completely dehydrating the acid. This is seen from the following determination of the water of crystallization.

1.9676 g. of the pulverized amorphous acid was heated in a steam bath for five hours; the loss in weight was 0.2116 g. It was further heated at 115° to constant weight. Total loss in weight, 0.2606 g.

	Found	Calc. ($C_9H_6O_5.2H_2O$)
H_2O	13.3	15.65

The acid thus contained 2.35% less water of crystallization than corresponds to the dihydrate.

Determination of Phthalonic Acid: Two methods were devised for the quantitative determination of phthalonic acid, both of which can be quickly and accurately carried out. In the first the carbon monoxide

[1] Ber. 31, 369, (1898).

[2] Ibid 370, (1898).

evolved on heating with sulphuric acid is measured, and in the second the phthalonic acid is oxidized by a volumetric solution of potassium permanganate.

First Method: The phthalonic acid, about 0.5 g., is placed in a thick-walled hard glass test tube; and 5 cc. concentrated sulphuric acid is added. The tube is then fitted with a rubber stopper through which pass two glass tubes, one running to within three quarters of an inch of the surface of the acid and connected with a carbon dioxide apparatus, *B*, the other ending just flush with the bottom of the stopper and connected to the inlet tube of a Schiff's azotometer, *C*, containing 30% caustic potash

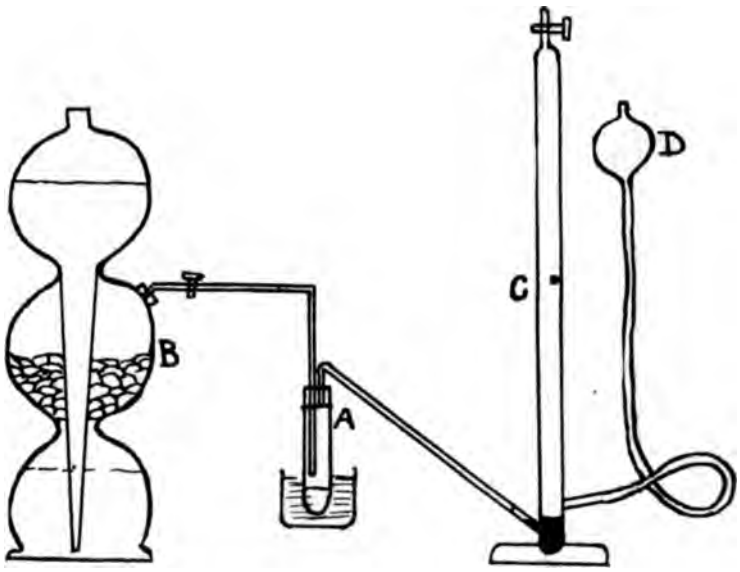

Fig. 1.

solution. The air is completely expelled by allowing a rapid stream of carbon dioxide to pass through the apparatus, the potash solution during this operation being almost all in the levelling bulb *D*. When the air is all expelled the tube of the azotometer is filled with the potash solution, and the levelling bulb placed so that the surface of the potash in it is about level with the inlet tube of the azotometer, the mixture of phthalonic acid and sulphuric acid is gradually heated in a paraffine bath to 130° when carbon monoxide is quite rapidly evolved. This continues for about ten minutes when the evolution slackens. The temperature is now raised to 140° and in five minutes more the greater part of the carbon monoxide is evolved. At this temperature carbon monoxide would continue to be evolved very slowly for six or seven hours; but if the temperature is raised to 180° the remaining gas is quickly given off, and

the evolution entirely ceases. The whole duration of the heating is about one hour. The carbon monoxide remaining in the reaction tube is driven over into the azotometer by a stream of carbon dioxide; the levelling bulb is raised so that the pressure inside the azotometer is slightly greater than that of the atmosphere, and the azotometer is disconnected from the heating tube. The gas is then transferred to a gas burette filled with a saturated solution of carbon monoxide in water, and after standing half an hour the volume is read, barometer and thermometer being noted. In each of two experiments an amount of carbon monoxide corresponding to 0.49 g. of phthalonic acid was obtained from 0.500 g. of the acid.

Another series of experiments showed that when phthalic acid or

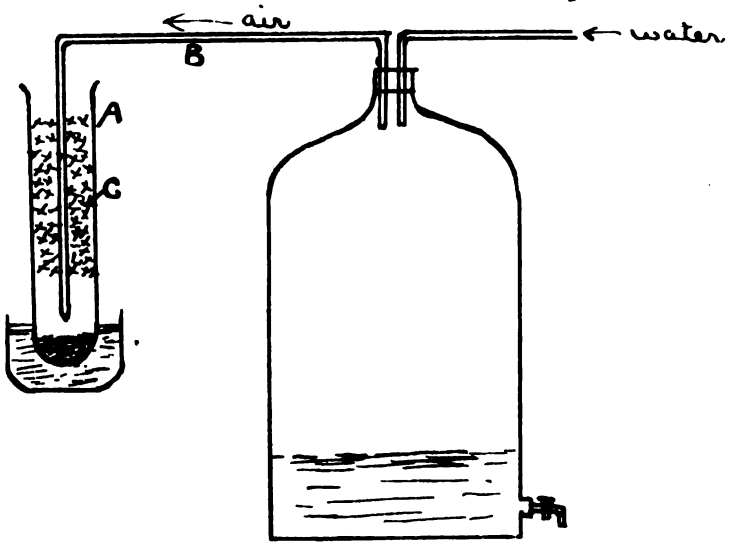

Fig. 2.

phthalic anhydride was heated with concentrated sulphuric acid to 210°, no gas not absorbed by caustic potash solution was evolved.

Second Method: This method, while just as accurate as the preceding has the advantage of being much more rapid; it allows the determination of phthalonic acid in the presence of phthalic, homophthalic, and phthalid-carbonic acids.

The phthalonic acid is dissolved in water, sulphuric acid added, and decinormal potassium permanganate run in from a burette. The oxidation is slow at first, but increases in speed as it proceeds, owing probably to the catalytic action of the manganous sulphate formed. The end point can best be obtained by running in an excess of permanganate and titrating back with ferrous sulphate until the last tinge of pink is discharged.

By working in this way the end point can be determined without difficulty within two drops of twentieth-normal ferrous sulphate. The results agreed accurately with the theory.

The titration must not be carried out in hot solutions, as in that case homophthalic, phthalid-carbonic, and even phthalic acids are acted on. By adding manganous sulphate to the phthalonic acid before running in the permanganate, the action of the latter is much accelerated.

Separation and Determination of Phthalic Acid: The method consists in separating the phthalic acid from homophthalic and phthalid-carbonic acids by sublimation, and determining it with volumetric alkali. The apparatus in which the sublimation is effected is made up of the test tube A, the air tube B, and the absorbent cotton C, to catch the sublimed phthalic anhydride. The tube B ends in a fine point about half an inch above the mixture of organic acids in the bottom of the test tube, and is connected with an inverted aspirator D.

The test tube is immersed to the depth of 3/4-inch in a metal bath kept at 200°–220°, and a fairly strong current of air directed on to the surface of the acids. After half an hour, the apparatus is removed from the bath. When cool, the bottom of the test tube is cut off, the cotton is transferred to a beaker and any anhydride adhering to the interior of A or the exterior of B is washed into the beaker by a volumetric solution of caustic potash. Excess of the potash is then added to the contents of the beaker, and after the cotton has soaked for half an hour in the alkaline solution, the excess of alkali is determined by volumetric sulphuric acid and phenol phthalein, boiling and taking the usual precautions to avoid errors due to carbon dioxide. A blank experiment showed that the "Bauer and Black cotton" used was perfectly neutral.

In this connection it should be noted, that phthalic anhydride cannot be determined by caustic potash in the presence of alcohol; even the alcohol contained in a few drops of phenolphthalein solution used as indicator affects the results, causing the red color to appear with too little potash, possibly due to the formation of an acid ester of phthalic acid. It is necessary, therefore, to introduce the indicator in the solid form, or dissolved in the volumetric potash.

The following results show the degree of accuracy of the method: Taken, 0.250 g. phthalic acid, 0.25 g. homophthalic acid and 0.25 g. phthalid-carbonic acid; found, 0.252 and 0.249 g. phthalic acid.

Fluorescein Reaction: This was carried out in the following manner: One decigram of resorcinol was mixed with its own weight or less of the acid to be tested, moistened in a test tube with one drop of concentrated sulphuric acid, and heated to 160° for three minutes in a bath of sulphuric acid. After cooling, the mass was shaken with 2 cc. of a 10 per cent. solution of caustic soda, and poured into 500 cc. of water.

When resorcinol alone is treated as described above, a red solution is obtained with marked blue fluoresence. One decigram of phthalic acid with the resorcinol gives a light solution with very strong green fluorescence; one milligram, a red solution with green fluorescence; and one-fifth milligram, a solution redder than the last, with blue-green fluorescence; on comparing it with the solution obtained from resorcinol alone, the green hue of the fluorescence is distinctly recognizable.

The following substances were also tested, one decigram being used in each case: naphthalene, red-pink solution, with green fluorescence; α-naphthoquinone, the same; β-naphthoquinone, dark green solution, no fluorescence; α-naphthol, red solution, blue fluorescence; β-naphthol, the same. In none of these cases was the fluorescence as marked as when one-fifth milligram of phthalic acid was employed. Phthalonic acid gave a dark red solution, with strong blue-green fluorescence; phthalid-carbonic acid, a pink-red solution with green fluorescence, much resembling that obtained from naphthalene; and homophthalic acid, a slightly red solution, with green fluorescence, almost as strong as when a decigram of phthalic acid was used.

I desire to express my thanks to Prof. W. Lash Miller under whose direction this work was performed.

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PROF. W. H. ELLIS IN THE CHAIR.

THE DETERIORATING EFFECT OF "ACID PICKLE" ON STEEL RODS, AND THEIR PARTIAL RESTORATION ON "BAKING."

BY HERBERT A. BAKER AND W. R. LANG.

It is the universal practice in wire manufacture to "pickle" the steel rods in order to remove the black scale of oxide before drawing them into wire. This has long been known to deteriorate the quality of the rods, but it has been found that, if the rods are "baked" at 250° F. for some hours after this treatment, they are in a great measure restored, and can then be drawn into wire. The following physical tests were made in order to find out quantitatively the amount of such deterioration and subsequent restoration of the rods. The work was done on samples taken in the different stages of the process of manufacture at the Imperial Steel and Wire Company's plant at Collingwood, Ontario, at the suggestion of the manager, Mr. J. A. Currie. Samples of three different coils of rods were taken in the following stages:—(1) Before treatment with acid; (2) after acid cleaning; (3) after rusting; (4) after lime coating; (5) after baking. Table I. shows the tensile strength, percentage elongation over 8 ins., and percentage contraction of the rods; the strength of the bath, time immersed, and time of baking are also given.

The tests were made with a Riehlé machine, by the kind permission and with the assistance of the staff in the Engineering Department, University of Toronto. It may be observed that the ultimate strength remains throughout the process as constant as can be expected of that kind of test. The percentage elongation over 8 ins. rather unexpectedly remains constant, but the sudden drop in the ability to contract to a small "neck," before breaking, occurs immediately after acid treatment, and remains practically constant until after "baking," when a marked recovery in this property occurs, the three rods agreeing well in this behaviour. It is important to note that on this property of "necking in," or contracting in area on stretching, depends the property of drawing well through

TABLE I.

Rod	Strength in lb. per sq. in.			Elongation over 8 ins.			Percentage contraction.		
	A	B	C	A	B	C	A	B	C
				per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Before treatment	65,700	59,700	69,100	16	13	12	63	66	67
After acid cleaning	61,400	59,700	64,200	16	13	13	38	44	47
„ rusting	62,800	57,000	64,700	17	14	11	38	47	44
„ lime coating	65,700	59,700	67,000	16	14	—	37	47	41
„ baking	65,700	58,000	67,600	16	13	—	57	66	56

The strengths of acid used, at 100° C., were : A, 38 per cent. ; B, 11 per cent. ; and C, 10 per cent. ; and the times of immersion in the baths : A, 1 hr. ; B, 45 mins. ; C, 1 hr. 10 mins. All the rods remained in the " baker " for about 4 hours.

the die, which is a conical hole in a block of tungsten steel.

This deterioration and recovery at the same stages in the process is also well shown in the following bending tests, which corroborate the contraction tests :—

TABLE II.

Bending tests on the rods.

	Before treatment.	After acid cleaning.	After rusting.	After lime coating.	After baking.
Rod A.	100	70	64	64	100
„ B.	100	60	56	57	99
„ C.	100	71	55	53	100

These figures are relative, of course, and express the ability to bend a certain number of times through a definite angle before breaking. They are the result of averaging eight or ten tests in each case. The highest number was taken as 100, and the rest calculated proportionately. The results show a break in the bending properties of the rod immediately after acid treatment, and a recovery after "baking," thus corresponding to the effect on the rods as indicated by the contraction tests.

Shearing tests were also made, but the differences were so small that no conclusions could be drawn from them.

An examination of the wires of different diameters drawn from these rods (correspondingly marked A, B, C) was also made in the same manner :—

TABLE III.

Tensile strength and percentage contraction of wires.

1. *Tensile strength.*

		Wires A.	Wires B.	Wires C.
	Diam. in.	lb. per sq. in.	lb. per sq. in.	lb. per sq. in.
(*a*)	0·175	72,900	93,700	93,700
(*b*)	0·142	112,600	113,900	113,900
(*c*)	0·112	117,300	122,400	122,400
(*d*)	0·091	—	138,400	131,000
(*e*)	0·072	137,000	150,000	150,000

2. *Percentage contraction.*

		per cent.	per cent.	per cent.
(*a*)	0·175	52.0	54	47
(*b*)	0·142	45·0	38	36
(*c*)	0·112	28·5	31	32
(*d*)	0·091	—	36	33
(*e*)	0·072	20·0	37	30

It will be observed that wires B and C have a higher tensile strength than wire A. Incidentally the increase of tensile strength on drawing out will be observed. The fall in contraction area percentage, as the diameter of the wires tested decreases, is not so great in B and C as it is in A. This means that these wires could probably be drawn through two more dies before annealing would be necessary, while wire A would, in all likelihood, stand no more drawing. Thus B and C appear to be the better wires. The only difference in the treatment of the rods was that rod A was cleaned in 38 per cent. sulphuric acid, while rods B and C were cleaned in 10 per cent. acid. They were all "baked" about four hours—longer than usual—and are probably restored as much as possible. The results indicate that strong acid causes an unnecessary amount of deterioration in the rod, and that only weaker acid should be employed.

Table IV. gives the comparative bending abilities of the wires: this also would indicate that wires B and C are the better.

TABLE IV.

Bending tests on the wires.

	Wire A.	Wire B.	Wire C.
Diam. in.			
(*a*) 0·175	91	100	100
(*b*) 0·142	90	97	100
(*c*) 0·112	89	100	83
(*d*) 0·091	—	100	80
(*e*) 0·072	86	100	94

Many superintendents of plants have attributed the deterioration to the presence of sulphur, knowing that sulphur renders steel "cold short." This appears to the authors to be highly improbable, as careful analyses show no difference in the sulphur content, which was 0·051 per cent. both before and after treatment. It seems much more probable that a "hydride" of iron is formed, as has often been suggested. Several tests confirmatory of this idea were obtained, but not sufficiently conclusive for present publication. The investigation is being continued.

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No. 64: THE OXIDATION OF NAPHTHALENE TO PHTHALONIC ACID BY ALKALINE SOLUTIONS OF PERMANGANATE, BY R. ARTHUR DALY

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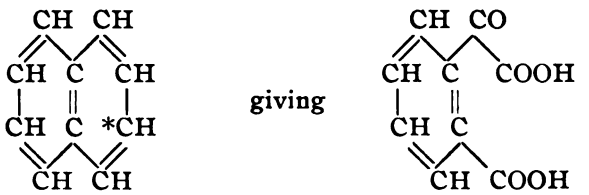
[THE MECHANISM OF THE OXIDATION OF NAPHTHALENE. I.]

THE OXIDATION OF NAPHTHALENE TO PHTHALONIC ACID BY ALKALINE SOLUTIONS OF PERMANGANATE

BY R. ARTHUR DALY

In 1894 Tcherniac[1] showed that naphthalene may readily be oxidized to phthalonic acid by the action of a boiling solution of potassium permanganate; and this reaction, which gives a yield of about 80 percent of the theoretical amount, has ever since been used as the best method of preparing that acid.[2]

The molecule of phthalonic acid contains but nine of the ten carbon atoms present in naphthalene, the tenth (marked with a star in the formula), being oxidized to CO_2 by the permanganate:



Naphthalene — Phthalonic acid

It is natural to suppose, however, that the phthalonic acid, although the product of the oxidation under the conditions of the method of preparation, is only the last of a number of compounds which have been formed and oxidized in turn. This supposition is supported by the fact that both α- and β-naphthol on treatment with potassium permanganate are converted into phthalonic acid;[3] and further by the existence of a large number of substances intermediate in composition between naphthalene and phthalonic acid, some of which—like α-naphtho-quinone[4]—may be prepared direct

[1] German patent 79693, March 23, 1894.

[2] Graebe und Trümpy: Ber. chem. Ges., Berlin, 31, 369 (1898).

[3] Henriques: Ibid., 21, 1608 (1888).

[4] Groves: Jour. Chem. Soc., 26, 209 (1873).

from the naphthalene by treatment with suitable oxidizing agents.

The experiments described in the following pages were undertaken in order to ascertain, if possible, which of the numerous intermediate compounds whose formulas suggest themselves may be regarded as actual stages in the formation of the phthalonic acid from the naphthalene, and which may not.

As phthalonic acid is a ketone, it seemed proper to begin the investigation with the corresponding secondary alcohol, and hydrocarbon. These are known as carboxy-mandelic acid (existing in the free form as the inner anhydride, phthalid-carbonic acid), and homophthalic acid, respectively.

$C_6H_4\begin{matrix}CO.COOH\\COOH\end{matrix}$	$C_6H_4\begin{matrix}CHOH.COOH\\COOH\end{matrix}$	$C_6H_4\begin{matrix}CH_2.COOH\\COOH\end{matrix}$
Phthalonic acid.	Carboxy-mandelic acid.	Homophthalic acid.

Neither of these has been detected in the product of the action of permanganate on naphthalene—it would indeed be difficult if not impossible to detect small quantities of them—but this is no proof that they were not first formed and then oxidized further.

Measurements of the rates at which naphthalene, homophthalic acid, and carboxy-mandelic acid are oxidized by potassium permanganate were accordingly undertaken, the idea being that if the two last named were really intermediate stages in the formation of phthalonic acid, they must be much more quickly oxidized than naphthalene itself, under the conditions which lead to a good yield of phthalonic acid.

The formation of phthalonic acid from naphthalene and potassium permanganate may be represented by the following gross chemical equation:

$$C_{10}H_8 + 16/3\ KMnO_4 = C_9H_6O_5 + CO_2 + H_2O + 16/3\ MnO_2 + 8/3K_2O.$$

As will be seen from this equation, the carbon dioxide formed in the reaction is not enough to neutralize the potash, so that the oxidation takes place in a solution which gradually

becomes more alkaline as the reaction proceeds, and whose alkalinity is apt to be affected by the formation of carbon dioxide in subsidiary reactions, for as noted above, the yield of phthalonic acid is only about 80 percent of the theoretical amount.

It was necessary, therefore, to see whether the degree of alkalinity affects the rate of oxidation of the naphthalene; and preliminary experiments were undertaken with this object in view.

Five grams of naphthalene and 25 cc of a decinormal solution of potassium permanganate were placed in each of four glass-stoppered bottles, which contained, respectively,

a 40 cc of decinormal potassium hydrate
b 40 cc decinormal sodium bicarbonate (8.4 grams per liter)
c 40 cc water
d 40 cc decinormal sulphuric acid

All the solutions were at the temperature of the room; the bottles were shaken for five hours and a half, and then the residual permanganate was determined. The analyses showed that in

a 14.9 cc permanganate had been reduced
b 11.5 cc " " " "
c 5.7 cc " " " "
d all the permanganate " " "

These figures prove that the degree of alkalinity of the solution has a very marked effect on the rate of the oxidation; all subsequent reactions were carried out in solutions containing sodium bicarbonate in such large quantity that the potash and carbon dioxide generated during the experiment could not materially alter the alkalinity of the solution.

Method of Determining the Permanganate

As the solutions in which the permanganate was to be determined contained (or might contain) phthalonic acid, and as this substance is quickly oxidized by permanganic acid, it seemed necessary to carry out the analysis in such a manner that no acid was added until the permanganate was destroyed.

A number of blank experiments showed that satisfactory results could be obtained by adding potassium iodide to the alkaline (bicarbonate) solution, which liberates iodine and precipitates manganese dioxide; and then acidifying, and determining the iodine with fiftieth-normal thiosulphate.

This method of working gives satisfactory results in the presence of homophthalic and phthalid-carbonic acids; but if phthalonic acid be present, an error of about 1 percent is introduced. If the acid and iodide be added simultaneously, however, in the form of a solution containing 0.4 gram potassium iodide 2 grams sulphuric acid and 110 cc water, the results are accurate; and as this second way of working gives good results in the presence of other acids as well, it was adopted in all cases.

I. RATE OF OXIDATION OF NAPHTHALENE

Method of Working

Five grams of naphthalene finely powdered, 25 cc decinormal permanganate, and 25 cc of a decinormal solution of sodium bicarbonate, were brought to the temperature of 40° C, mixed in each of eight wide-mouthed glass-stoppered 100 cc bottles, and shaken in a thermostat for periods varying from 30 minutes to four hours and a half.

As each was removed from the bath, its contents were poured into a quarter liter measuring flask containing about 60 cc of ice water, which was then filled to the mark with water of the temperature of the room. This stopped the reaction. The dilute solution was filtered through ordinary analytical filter paper, rejecting the first 30 or 40 cc of the filtrate to avoid error due to the action of the permanganate on the paper. (Hardened filters have less action on the permanganate, but the filtration lasts longer, and blank experiments showed that the method as described is satisfactory).

In fifty cubic centimeters of the filtrate, the permanganate was determined as described above; and in a second portion of 50 cc, the phthalonic acid.

Determination of Phthalonic Acid

To the fifty cubic centimeters of the filtrate, was added about 50 cc 2 percent sulphuric acid, and a few drops of F/10 manganous sulphate.[1] After standing for two minutes, during which the whole of the phthalonic acid is oxidized to phthalic acid and a brown precipitate is formed, the mixture of potassium iodide, sulphuric acid and water given on page 96 is added, and the iodine determined by fiftieth-normal thiosulphate. This method of analysis, for which I am indebted to Mr. Boswell, gives accurate results in the presence of homophthalic and phthalid-carbonic acids; if the mixture is let stand for longer than two minutes before adding the hydriodic acid, however, a correction has to be made for oxidation of phthalid-carbonic acid.

Method of Recording the Results of the Analyses

Let x represent the number of cubic centimeters of decinormal[2] permanganate reduced in alkaline solution during the experiment; and y the additional number reduced in acid solution by the phthalonic acid during the analysis. A is the permanganate initially present, in the same units.

Then the number of cubic centimeters of fiftieth-normal thiosulphate used in the permanganate determination (page 96), divided by five, and multiplied by the ratio between the whole volume of the solution and the part taken for analysis, given $A - x$; whence, if A be known, x can be obtained.

The number of cubic centimeters of fiftieth-normal thiosulphate used in the phthalonic acid determination (page 97), divided by five, and multiplied by the volume ratio, gives $A - x - y$.

These relations hold only if the manganese dioxide be removed before the analyses, as prescribed on page 96. In certain cases this is not possible, and the oxidizing value of the dioxide in acid solutions has to be reckoned with. The "permanganate determination" then gives $A - 0.6x$, and

[1] One-tenth formula-weight per liter.

[2] One-fiftieth formula-weight $KMnO_4$ per liter.

the "phthalonic determination" gives $A - 0.6x - y$. In both cases the difference between the two determinations gives y.

Results of the Measurements of the Rate of Oxidation of Naphthalene

The results of the measurements are arranged in tables, at the head of which are given the amounts of the various reagents taken, under t is given the duration of the oxidation in hours; under $A - x$ the residual permanganate (calculated for the whole bottle full). and under x the permanganate reduced, in cubic centimeters of decinormal solution. In all cases the temperature was 40° C; the permanganate solution "Pm," and the sodium bicarbonate,[1] "Bicarb" were decinormal. The titre of the permanganate changed somewhat; the accurate value is given after "A."

TABLE I

Naph., 5 gram ; Bicarb., 25 cc ; Pm., 25 cc; $A = 24.9$

t	$A - x$	x	x/t
0.5	23.1	1.8	3.6
1.0	21.3	3.6	3.6
1.75	17.4	7.5	4.3
2.33	14.1	10.8	4.6
3.33	10.4	14.5	4.4
4.5	6.3	18.6	4.1

As will be seen from the table, the rate at which the naphthalene is oxidized is as great when the permanganate is three-quarters reduced as it is at the beginning of the experiment. This suggested that, perhaps, the manganese dioxide which is precipitated at the end of the first hour might affect the rate; and a second series of experiments was undertaken, in which manganese dioxide was added at the beginning.

The "manganese mud" used was prepared by mixing 320 cc of decinormal permanganate, with 96 cc of a solution of manganous sulphate containing one formula-weight $MnSO_4$ in ten liters, and 400 cc fifth-normal sodium bicarbonate

[1] 8.4 grams per liter.

Twenty-five cubic centimeters of this mixture contain as much manganese dioxide as would be formed by the reduction of 25 cc of the permanganate by naphthalene, and 0.75 times as much sodium bicarbonate as in 25 cc of the $n/10$ "bicarb" solution. Special experiments showed that, in the absence of permanganate, this "mud" is without action on naphthalene.

TABLE II

Naph., 5 gram; Mangan. mud, 25 cc; Pm., 25 cc; $A = 23.1$

t	$A-x$	x	x/t	$A-x-y$	y	$40y/3$
1	18.57	4.54	4.5	18.6	0.35	4.66
2	13.84	9.27	4.6	13.5	0.62	8.3
3	9.62	13.48	4.5	8.95	0.85	11.3
4.75	4.26	18.84	4.0	3.2	1.15	15.3

In these experiments the rate, x/t, is much more constant than in those of Table I; in particular, the increase after the first hour has disappeared.[1] The addition of the mud has therefore simplified matters, and it has been added in all subsequent experiments.

The Product of the Oxidation of the Naphthalene in the Experiments of Table II

Under $A-x-y$, in column 5 of Table II, is entered the amount of permanganate left after acidifying the filtrate and standing for two minutes, as described under "determination of phthalonic acid" on page 97. The difference between the second and fifth columns therefore gives the amount of permanganate reduced in the acid solution, presumably by phthalonic acid.

If the reaction between naphthalene and permanganate in alkaline solution takes place according to the equation given on page 94, then for every mol of naphthalene oxidized,

[1] A number of experiments were made to study the effect of the concentration of the permanganate on the rate of oxidation of naphthalene. As this matter is apart from the main purpose of the present paper the results are not given here.

one mol of phthalonic acid will be formed, and 16/3 mol permanganate or 80/3 liters of normal solution will be required.

The oxidation of phthalonic acid to phthalic acid, however, as carried out in the analyses, takes place in acid solution, according to the equation:

$$C_9H_6O_5 + 2/5\ KMnO_4 + 3/5\ H_2SO_4 = 1/5\ K_2SO_4 + 2/5\ MnSO_4 + 3/5\ H_2O + C_8H_6O_4$$

Thus every mol of phthalonic acid oxidized by the acid permanganate reduces 2/5 mol of the latter, or two liters of normal solution. From these calculations it appears, that if the naphthalene be oxidized to phthalonic acid in the alkaline solution, and if the subsequent reduction of the permanganate in acid solution is due exclusively to the phthalonic acid so formed, then for every cubic centimeter reduced in acid solution 40/3 cc must have disappeared in the alkaline solution. The last column of Table II gives the values of $40y/3$, and it will be seen that they agree very closely in value with those of x, the permanganate reduced in the alkaline solution. In each case the phthalonic acid formed in a little less than that corresponding to the naphthalene oxidized; but this is only what might be expected, as even in alkaline solution the phthalonic acid is slowly acted on by permanganate.

The agreement between the numbers in the third and seventh columns of the table thus shows that the main product of the oxidation in alkaline solution, under the conditions of my experiments, is phthalonic acid.

II. RATE OF OXIDATION OF HOMOPHTHALIC ACID

The experiments were carried out in the same manner as those with naphthalene; homophthalic acid solution was made up by neutralizing 1 gram of the acid with sodium bicarbonate, and making up the volume to 100 cc with water.

TABLE III

Homoph. soln., 5 cc; Mud, 20 cc; Pm., 25 cc; $A = 23.2$

t	$A-x$	x	$A-x-y$	y	$10y/3$
1	22.5	0.7	22.4	0.1	0.33
2	22.1	1.1	21.98	0.12	0.4
3	21.65	1.65	21.5	0.15	0.5

The homophthalic acid present was enough to reduce about 19 cc of the permanganate in alkaline solution, if it itself were oxidized to phthalonic acid.

Two points are to be noticed in the results of these determinations. In the first place, the yield of phthalonic acid is only half or one-third of that corresponding to the permanganate reduced by the homophthalic acid, as may be seen by comparing the numbers under x with those under $10y/3$. This discrepancy may possibly be due in part to the difficulty of determining such small quantities with accuracy, but is nevertheless worth noting.

The second point is the extreme slowness with which the homophthalic acid is acted on by the permanganate. As it seemed possible that this oxidation might be accelerated by the simultaneous oxidation of naphthalene, after the manner of the "induced reactions," a parallel series of experiments was carried out in which both naphthalene and homophthalic acid were oxidized together, and the amount of homophthalic acid acted on was arrived at by subtracting the permanganate reduced by the naphthalene as determined in Table II. The results of these experiments and calculations, which are naturally strongly affected by the unavoidable errors of manipulation and method, were in full accord with those of Table III, and showed clearly that the simultaneous oxidation of naphthalene causes no acceleration in the oxidation of homophthalic acid.

According to the experiments of Table II, 13.48 cc of permanganate are reduced in three hours by naphthalene, which itself is converted almost quantitatively into phthalonic acid. If homophthalic acid were one of the intermediate products, enough must have been formed to reduce one-quarter of 13.48, or 3.37 cc of permanganate on its subsequent oxidation to phthalonic acid. The experiments of Table III show, however, that even with a relatively high concentration of homophthalic acid, less than half that amount is oxidized in the three hours. They thus definitely exclude the possibility that homophthalic acid is one of the

intermediate compounds produced during the oxidation of naphthalene to phthalonic acid by potassium permanganate.

III. RATE OF OXIDATION OF *o*-CARBOXY-MANDELIC ACID

A solution of the sodium salt of this acid was prepared by neutralizing 1 gram of phthalid-carbonic acid with sodium bicarbonate, and making up to 100 cc with water. Five cubic centimeters of this solution would require 9.95 cc of my permanganate to oxidize it in alkaline solution to phthalonic acid.

TABLE IV

Carbox. soln., 5 cc; Mud, 20 cc; Pm., 25 cc; $A = 23.1$

t	$A-x$	x	$A-x-y$	y	$5y/3$	K
0.5	22.2	0.9	21.8	0.4	0.66	0.082
1.0	21.2	1.9	20.35	0.85	1.4	0.092
1.75	20.6	2.5	18.25	2.35	2.25	0.072
2.5	20.1	3.0	18.3	1.8	3.0	0.062
3.5	19.15	3.95	17.0	2.15	3.6	0.062
4.5	18.45	4.65	15.9	2.55	4.25	0.062

TABLE V

Carbox. soln., 10 cc; Mud, 15 cc; Pm., 25 cc; $A = 23.63$

t	$A-x$	x	$A-x-y$	y	$5y/3$	K
0.5	21.23	2.4	19.5	1.65*	2.75	0.12
1.25	19.24	4.39	16.62	2.62	4.36	0.086
2.25	17.2	6.43	13.0	4.2*	7.0	0.075
3.37	15.38	8.25	10.42	4.96	8.25	0.064

The values of K in the last columns of Tables IV and V have been calculated from x and t by the formula

$$K = \log_{10} \frac{B}{B-x}$$

in which B is the amount of permanganate equivalent to the carboxy-mandelic acid initially present; that is, 9.95 in Table IV, and 19.9 in Table V.

The agreement between $5y/3$ and x, shows that the product of oxidation of the carboxy-mandelic acid is phthalonic acid; and the agreement between the values of K in

the two tables shows that the rate of oxidation is proportional to the concentration of the carboxy-mandelic acid. The decrease of K as the reaction proceeds is due, no doubt, to the fall in concentration of the permanganate, while the irregular values of y in Table V, which are marked by an asterisk, are due to two faulty analyses in which the acidified solution was let stand longer than two minutes before adding the hydriodic acid (see page 97).

As in the case of the homophthalic acid, a series of measurements was carried out to see whether the simultaneous oxidation of naphthalene accelerated the action of permanganate on the carboxy-mandelic acid. This was found not to be the case.

These results in connection with those of Table I, are sufficient to show that carboxy-mandelic acid can not be one of the intermediate substances formed during the oxidation of naphthalene to phthalonic acid.

In three hours naphthalene reduced 13.48 cc of permanganate; if carboxy-mandelic acid were formed, one-eighth of the 13.48 cc, or 1.69 cc of the permanganate must have been employed to oxidize the latter to phthalonic acid. In the experiments of Table IV, about 3.5 cc of permanganate were reduced in the same time, and in Table V, about 7.0 cc. At first sight, therefore, the intermediate formation of carboxy-mandelic acid seems possible; closer inspection, however, shows that this is not the case. In the naphthalene experiments (Table II), 4.5 cc of permanganate were reduced per hour, which, on the hypothesis under consideration, means that 0.56 cc of permanganate per hour are reduced by carboxy-mandelic acid. As the rate of oxidation of the latter is proportional to its concentration in the solution, it follows (from Table V) that the amount constantly present in the 50 cc, must be equivalent to $0.56/1.9 \times 9.3 = 2.7$ cc permanganate. To form this much of the carboxy acid from naphthalene would require 18.9 cc permanganate; and until this amount of permanganate had been reduced, the formation of phthalonic

acid could not take place at the rate observed. In point of fact, however, the rate 4.5 cc per hour is attained in the very first hour, when not one-quarter of 18.9 cc permanganate has been reduced, so that the hypothesis that carboxy-mandelic acid is one of the intermediate substances formed during the oxidation of the naphthalene must be definitely rejected.

IV. RATE OF OXIDATION OF *o*-CARBOXY-BENZOYL-ACETIC ACID

Having thus shown that the substances which stand in the closest relation to phthalonic acid can not be considered as intermediate stages in its formation from naphthalene, I took up the study of *o*-carboxy-benzoylacetic acid, and then made a few experiments with the two naphthoquinones, both of which I find are readily oxidized to phthalic acid by permanganate in acid solution, and one of which has been prepared from naphthalene by the action of chromic acid.

TABLE VI

Phthal.-acet. acid, 0.0100 gram; Bicarb., 0.15 normal, 25 cc; Pm., 25 cc; $A = 24$

t	$A-x$	x	$A-x-y$	y
0.25	19.90	4.9	18.85	1.05
0.50	19.30	5.5	18.20	1.10
1.00	19.40	5.4	18.35	1.05
2.00	19.48	5.3	18.45	1.03
3.00	18.80	6.0	17.75	1.05

The 0.0100 gram of phthalyl-acetic acid (inner anhydride of the *o*-carboxy acid) employed in the experiments, would require 5.3 cc decinormal permanganate to oxidize it to phthalonic acid in alkaline solution; and the phthalonic acid so formed would be further oxidized in acid solution to phthalic acid by 1.06 cc of the permanganate.

As Table VI shows, these amounts of permanganate were reduced in the first half hour; so far as these rate measurements go, then, *o*-carboxy-benzoylacetic acid may be regarded as one of the intermediate stages in the oxidation of naphthalene;

but neither homophthalic nor *o*-carboxy-mandelic acid can be formed during the oxidation of *o*-carboxy-benzoylacetic acid to phthalonic.

V. RATE OF OXIDATION OF β-NAPHTHOQUINONE

The β-quinone is slightly soluble in decinormal sodium bicarbonate, giving a dark red solution from which it cannot be extracted by ether; after acidifying, however, the naphthoquinone may be ethered out, unchanged.

The solution in bicarbonate is very dilute; and, in consequence, the amount of permanganate reduced was small. It was therefore decided to dispense with filtration in making the analyses, for fear that the error due to the action of permanganate on the paper might be large enough to affect the result.

TABLE VII

Quin. soln., 30 cc; filtrate from "mud," 10 cc; Pm., 10 cc; $A = 10$

t	$A - 0.6x$	$A - 0.6x - y$	x	$5y/3$
0.25	8.6	—	2.3	—
0.50	8.45	—	2.6	—
0.75	8.4	7.61	2.7	1.32
1.0	8.35	7.5	2.7	1.42

As will be seen from the table, the amount of oxygen needed to oxidize the quinone in alkaline solution, (x), is just double that required to oxidize the product of that oxidation to phthalic acid ($5y/3$). In other experiments, in which the quinone was shaken with sodium bicarbonate solution and permanganate, the values of $5y/3$ were about one-third those of x. These numbers cannot be reconciled with the hypothesis that phthalonic acid is the product of the oxidation of the quinone; they suggest rather the formation of the diketo-dibasic acid $C_6H_4(CO.COOH)_2$. No account of this substance can be found in the literature; and attempts to prepare it, by acting on phthalyl chloride with potassium or mercuric cyanides and saponifying the nitrile, have not as yet led to the desired result.

VI. RATE OF OXIDATION OF α-NAPHTHOQUINONE

To convert one mol of the quinone to phthalonic acid requires five atoms of oxygen, and a sixth is necessary to complete the oxidation to phthalic acid. For every cubic centimeter of permanganate reduced in acid solution, 25/3 should be reduced in alkaline.

TABLE VIII

Quinone, 0.0166 gram; Bicarb., 25 cc; Pm., 25 cc; $A = 24.80$

t	$A-x$	x	$A-x-y$	y	$25y/3$	y calc.	x calc.
0.25	11.75	13.05	9.70	2.05	17.1	2.10	17.5

As the quinone is insoluble in the bicarbonate solution, it is possible that part of it became coated with dioxide, and was thus protected from oxidation until acid was added, which would account for x being less than $25y/3$. This experiment, therefore, leaves it quite possible that α-naphthoquinone is a stage in the oxidation of naphthalene to phthalonic acid; while the rapidity of the oxidation precludes the possibility of either homophthalic or *o*-carboxy-mandelic acids being stages in the oxidation of the quinone.

CONCLUSION

The experiments described in this paper are of interest as laying the foundation of a method for studying the mechanism of complex organic reactions.

In the special case selected for study, they show conclusively that homophthalic acid and carboxy-mandelic acid are not intermediate stages in the formation of phthalonic acid by the action of alkaline solutions of potassium permanganate on naphthalene, on phthalyl acetic acid, or on the naphthoquinones; β-naphthoquinone is probably not an intermediate stage in the oxidation of naphthalene, while *o*-carboxy-benzoylacetic acid and α-naphthoquinone may be.

In conclusion, my thanks are due to Prof. W. Lash Miller at whose suggestion this research was undertaken, and under whose supervision it was carried out.

University of Toronto,
December, 1906.

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THE REACTION BETWEEN BROMIC, HYDRIODIC AND ARSENIOUS ACIDS, AND THE "INDUCTION" BY HYDROGEN BROMIDE OF THE REACTION BETWEEN BROMIC AND ARSENIOUS ACIDS

BY FRED C. BOWMAN

The reduction of bromates by bromides or iodides in acid solution has been studied by Ostwald,[1] Burchard,[2] Meyerhoffer,[3] Scott and Noyes,[4] Magnanini,[5] Judson and Walker,[6] Schilow,[7] and lastly by Mr. R. H. Clark.[8] The net result of these researches is that the rate is proportional to the first power of the concentration of the bromate, the first power of that of the bromide or iodide, and the second power of that of the acid.

The ordinary chemical equations for the reactions of the bromate with the bromide and iodide are:

$$\begin{aligned} KBrO_3 + 5KBr + 3H_2SO_4 &= 3K_2SO_4 + 3Br_2 + 3H_2O \\ KBrO_3 + 6KI + 3H_2SO_4 &= 3K_2SO_4 + 3I_2 + 3H_2O + KBr \end{aligned} \quad (1)$$

or in the ionic notation:

$$\begin{aligned} BrO'_3 + 9Br' + 6H^{\bullet} &= Br' + 3Br'_3 + 3H_2O \\ BrO'_3 + 9I' + 6H^{\bullet} &= Br' + 3I'_3 + 3H_2O \end{aligned} \quad (2)$$

Since these do not square with the kinetic hypothesis, which demands equations of the form

$$BrO'_3 + Br' + 2H^{\bullet} = \text{(products of the reaction)} \quad (3)$$

resort has been had to the usual method of "explaining" discrepancies between theory and practice in kinetic measurements, by assuming the temporary existence of hypothetical

[1] Zeit. phys. Chem., **2**, 127 (1888).
[2] Ibid., **2**, 796 (1888).
[3] Ibid., **2**, 585 (1888).
[4] Ibid., **18**, 128 (1895).
[5] Gazz. chim. Ital., **20**, 390 (1890).
[6] Jour. Chem. Soc., **73**, 410 (1898).
[7] Zeit. phys. Chem., **27**, 512 (1898); **42**, 641 (1903).
[8] Jour. Phys. Chem., **10**, 679 (1906).

intermediate compounds, such as the HBrO and $HBrO_2$ of the following equation.

$$\begin{aligned} BrO'_3 + Br' + 2H^{\bullet} &= HBrO_2 + HBrO \\ BrO'_3 + I \quad + 2H \quad &= HBrO_2 + HIO \end{aligned} \qquad (4)$$

Independent evidence of the formation of these intermediate acids would, of course, be very welcome;[1] and even the confirmation by experiment of conclusions based on the assumption that they exist would be of value.

One such conclusion has been drawn by Luther,[2] who points out that compounds which *ex hypothesi* react quickly with certain reducing agents, may naturally be expected to react quickly with others; and suggests that new cases of chemical induction are apt to be found by a study of the reactions whose kinetic equations lead to the assumption of such hypothetical "primary" products.

The only induced reaction in which bromic and hydrobromic acids are known to take part, is that in which arsenious acid acts as acceptor; and, in accordance with the view just set forth, the induction is ascribed—both by Luther and by Schilow who discovered the reaction—to the oxidation of the arsenious acid by the hypothetical primary products of Equation 4.

It is not necessary, however, to have recourse to these hypothetical acids in order to account for the results of Schilow's measurements. The bromine liberated by the oxidation of the hydrogen bromide (Equation 1) acts instantaneously on arsenious acid, and all the experimental data are in full accord with the assumption that the "induced" oxidation of arsenious acid is due to this action alone.[3] There are thus two explanations of Schilow's measurements available. The first of them is in accordance with the explanation offered for the kinetics of the reaction between bromic and hydrobromic acids, and at first sight seems to afford it independent support; but the second accounts for all that is known of the induction

[1] Ostwald: Lehrbuch II, (2) 243 (1902).

[2] Zeit. phys. Chem., **46**, 817 (1903).

[3] Ibid., **42**, 670 (1903).

without the assumption of any hypothetical mechanism whatever.

In order to throw more light on the matter, I have studied the oxidation of arsenious acid in solutions containing bromic and hydriodic acids. In this case, the final product—iodine—does not react instantaneously with the arsenious acid, but slowly, according to known laws; so that if any arsenious acid were oxidized by the hypothetical intermediate acids, or in any other way than by the iodine formed in the reaction, the fact could be established, and the amount ascertained. My work has been much facilitated by the circumstance that the reaction between bromic and hydriodic acid and that between arsenious acid and iodine have already been studied in this laboratory by Mr. Clark[1] and Mr. Roebuck[2] respectively. This has enabled me to plan my experiments so that very little arsenious acid was oxidized by the iodine; any action of the hypothetical oxyacids would therefore readily be detected.

The reaction was carried out in a thermostat at 0° to 0.2°; the burettes and pipettes were calibrated by myself, and the solutions of arsenious acid, potassium iodide, potassium bromate, iodine and sodium thiosulphate were made from pure chemicals and standardized in the usual way. The iodide in the iodine solution was allowed for in calculating the concentration of the iodion.

In the tables and in the calculations, the amount of each reagent is expressed in cubic centimeters of hundredth-normal solution. Thus the number after $KBrO_3$ multiplied by $^1/_6 \times 167.1 \times 10^{-5}$ gives the number of grams of potassium bromate; the number after KI multiplied by $^3/_2 \times 166 \times 10^{-5}$ gives the number of grams of potassium iodide; the number after KBr multiplied by $^3/_2 \times 119.1 \times 10^{-5}$ gives the number of grams of potassium bromide; the number after H_2SO_4, multiplied by $^1/_2 \times 98.08 \times 10^{-5}$ gives the number of grams of sulphuric acid; the number after I multi-

[1] Jour. Phys. Chem., 10, 679 (1906).
[2] Ibid., 6, 365 (1902); 9, 727 (1905).

plied by 126.85×10^{-5} gives the number of grams of free iodine, and that after As_2O_3 multiplied by $^1/_4 \times 198 \times 10^{-5}$ the number of grams of arsenious acid. After *Vol.* is given the volume in liters in which these amounts of the reagents were dissolved.

The duration of the reaction, in minutes, is stated under t; the number of grams of bromate reduced may be found by multiplying the number under x by $^1/_6 \times 167.1 \times 10^{-5}$; and the number of grams of arsenious acid oxidized to arsenic acid, by multiplying the number under y by $^1/_4 \times 198 \times 10^{-5}$. In solutions containing both bromate and arsenious acid, therefore, the quantity of free iodine in the solution is represented by $x - y$.

The measurements fall naturally into three series.

Series I. The Effect of Arsenious Acid on the Reaction between Bromic and Hydriodic Acids

First of all it was necessary to know whether addition of arsenious acid affects the rate at which bromic acid is reduced by hydrogen iodide. For this purpose parallel sets of measurements were made, one in the presence of arsenious acid and one in its absence, all the other reagents being of the same concentrations in both.

The solutions of potassium bromate, potassium iodide and sulphuric acid were mixed in a large stoppered bottle, and at intervals samples were pipetted out, rendered alkaline with ammonium bicarbonate, and titrated with centinormal arsenious acid. The measurements are recorded in Tables I, II and III.

From each pair of numbers (x, t) so obtained, the value of the constant K_1 of the equation[1]

$$dx/dt = K_1(KBrO_3 - x)(KI - x)(H_2SO_4 - x)^2(Vol)^{-3} \qquad (5)$$

was calculated as follows. A curve was plotted on section paper with x and the right hand member of Equation 5 as coördinates, and the areas under the curve were measured. For each value of x the corresponding value of

[1] Clark : loc. cit.

$$K_1(\text{Vol})^{-3} \int dt/dx.dx = K_1 t(\text{Vol})^{-3} \qquad (6)$$

was thus obtained; and from this the value of K_1 itself, by division by $(Vol)^{-3}$ t. This method, which was suggested by Prof. Lash Miller, is perhaps the easiest way to determine K from a series of values of x and t, when the form of the differential equation is known.

TABLE I

$KBrO_3$, 199; KI, 1984; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
6	4.68	974
19	11.76	989
30	15.50	997
40	17.92	997
50	19.58	945
60	20.73	969
70	21.77	980
80	22.48	982
90	22.82	930
100	23.68	1041
	Average	980

TABLE II

$KBrO_3$, 199; KI, 1984; H_2SO_4, 4000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
3	7.40	805
6	12.37	825
9	15.73	807
12	18.18	809
15	19.87	809
18	21.25	823
21	22.15	798
	Average	810

TABLE III

$KBrO_3$, 199; KI, 3968; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
5	6.95	928
10	11.52	905
15	14.84	903
20	17.28	901
25	19.17	909
30	20.42	909
	Average	909

Comparison of Tables I, II and III with Tables VIII, IX and X

t	x		$K_1 \times 10^{15}$	
	I	VIII	I	VIII
6	4.68	4.82	974	—
12	(8.41)	8.34	—	—
18	(11.25)	11.13	—	—
24	(13.62)	13.59	—	—
30	15.50	15.31	997	977
36	(16.98)	16.88	—	—
42	18.28	18.38	—	—
		Average	980	984

t	x		$K_1 \times 10^{15}$	
	II	IX	II	IX
3	7.40	7.45	805	828
6	12.37	12.07	825	797
9	15.73	15.44	807	789
12	18.18	17.99	809	793
15	19.87	19.81	809	796
18	21.25	21.05	823	783
21	22.15	22.63	798	—
		Average	810	798

t	x		$K_1 \times 10^{15}$	
	III	X	III	X
5	6.95	7.08	928	—
10	11.52	11.75	905	935
15	14.84	14.90	903	909
20	17.28	17.43	901	917
25	19.17	19.15	909	901
30	20 42	20.55	909	911
		Average	909	911

When arsenious acid is present (Tables VIII, IX and X) the kinetic equation must be modified somewhat, because of the regeneration of acid and iodide by the action of iodine on arsenious acid:

$$HAsO_3 + I_2 + H_2O = HAsO_4 + 2HI \qquad (7)$$

The amount of iodide present at any moment is thus no longer represented by $KI-x$, as in Equation 5, but by $KI-\overline{x-y}$, where y is the number of units of arsenious acid oxidized; similarly the acid present at any moment is given by $H_2SO_4-\overline{x-y}$. Thus the kinetic equation becomes:

$$dx/dt = K_1(KBrO_3 - x)(KI-\overline{x-y})(H_2SO_4-\overline{x-y})^2(Vol)^{-3} \qquad (8)$$

As in my experiments both KI and H_2SO_4 were large in comparison with x and y, the terms $KI-x-y$ and H_2SO_4-

$\overline{x-y}$ were nearly constant, and it was found convenient to replace them by their "effective averages" determined as follows at the suggestion of Mr. R. E. DeLury.[1] A curve was plotted with $x-y$ as ordinates and t as abscissae, using the values found by experiment. The area under this curve between $t = 0$ and $t = t'$, divided by t', is the "effective average" of $x-y$ from the beginning of the experiment to the moment t_1. This function may be written $X-Y$, and is defined by the relation:

$$X-Y=\frac{1}{t'}\int_0^{t'}\overline{x-y}\,dt \qquad (9)$$

Introducing these "effective averages" into Equation 8, and integrating:

$$K_1t'(KI-\overline{X-Y})(H_2SO_4-\overline{X-Y})^2\ (Vol)^{-3}=log\ nat\ \frac{KBrO_3}{KBrO_3-x} \qquad (10)$$

The values of K_1 entered in Tables VIII, IX and X were calculated from x and t by means of this equation.

The values of K_1 so obtained from experiments in which arsenious acid was present and from others in which it was not, are collected after Table III; the comparison shows clearly that the rate at which bromic acid is reduced by hydriodic acid is not affected by the presence of arsenious acid, and that the slight apparent acceleration is due to the formation of acid and iodide which accompanied the oxidation of the arsenious acid.

Series II. The Oxidation of Arsenious Acid by Iodine and the Effect of Hydrobromic Acid on the Rate of this Reaction

The rate of the reaction between arsenious acid and iodine has been thoroughly studied by Roebuck; but as my experiments were made with concentrations outside the range of Roebuck's measurements, I thought it better to undertake a new series of my own, rather than rely on an extrapolation from his tables. New measurements were also needed to

[1] See Jour. Phys. Chem., 10, 423 (1906).

ascertain what effect, if any, the presence of bromides might exert on the rate.

The solutions were mixed in a stoppered bottle, and at intervals a sample was pipetted out and analyzed. The method of analysis was that used by Roebuck, *viz.*, rapid titration with centi-normal thiosulphate without dilution or neutralization.

TABLE IV

As_2O_3, 200; KI, 2197; I, 198; H_2SO_4, 2000; Vol., 0.600
(50 cc titrated)

t	$I-y$ in 50 cc	$K_2 \times 10^{-4}$
2	15.68	169
7	14.88	154
12	14.08	159
17	13.44	155
22	13.03	140
27	12.67	133
32	12.27	130
37	11.56	142
42	11.06	145
52	10.41	143
72	9.27	140

TABLE V

As_2O_3, 200; KI, 2250; I, 247.3; H_2SO_4, 4002; Vol., 0.600
(50 cc titrated)

t	$I-y$ in 50 cc	$K_2 \times 10^{-4}$
16	18.75	177
30	17.51	166
45	16.65	159
60	15.70	156
75	14.95	156
90	14.25	152
105	13.68	151
120	13.15	150
135	12.64	150
150	12.17	150

TABLE VI

As_2O_3, 200; KI, 3968; I, 197; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	$I-y$ in 75 cc	$K_2 \times 10^{-4}$
30	22.58	132
60	20.92	135
90	19.34	135
120	18.11	133
150	17.03	133
180	15.96	136
	Average	134

Table IV contains measurements with solutions of approximately the same concentrations as those of Table VIII

in which bromic acid was used. Similarly Table V is parallel to Table IX and Table VI to Table X. The experiments of Table VI*A* were undertaken to find whether the decrease in the constant[1] K_2 of the kinetic equation[2]

$$dy/dt = \frac{K_2(I-y)(As_2O_3-y)(Vol)^2}{(KI-y)^2(H_2SO_4-y)} \qquad (11)$$

was due to the fall in the concentration of the iodine or to that of the arsenious acid.

TABLE VI*A*

As_2O_3, 100; I, 197; KI, 1984; H_2SO_4, 4000; Vol., 0.600 (75 cc titrated)

t	$I-y$ in 75 cc	$K_2 \times 10^{-4}$
20	23.31	—
40	22.03	—
60	20.92	155
80	20.17	142
100	19.29	145
120	18.61	143
140	18.11	143

TABLE VII

As_2O_3, 200; I, 247.5; KI, 2250; H_2SO_4, 4002; KBr, 200; Vol., 0.600 (50 cc titrated)

t	$I-y$ in 50 cc	$K_2 \times 10^{-4}$
45	16.92	139
60	16.08	139
75	15.25	140
90	14.52	141
105	13.92	138
120	13.52	133
135	13.00	135
150	12.52	136

Table VII contains the results of measurements made in solutions containing six times as much bromide as was formed from the bromate in any of my experiments. The rate is noticeably (10-15 percent) less than in the experiments of Table V in which—apart from the bromide—the concentrations were the same; but it is evident that the retardation due to the bromide formed during an experiment may be neglected.

Further measurements of the rate of oxidation of arsenious acid by iodine are furnished by the latter part of Table IX; for although bromic acid was present initially, it was practically all reduced in the first half hour, and from then on the only

[1] K_2 was computed in the same manner as K_1 of Tables I and II, by plotting a curve with y as abscissae and $K_2(Vol)^2dt/dy$ as ordinates.

[2] Roebuck: loc. cit.

reaction taking place in the solution was the oxidation of arsenious acid by iodine. The constant K_2 in Table IX was thus determined for the very solution in which the bromic acid had been reduced, $t = 70$ was taken as the initial point.

Series III. The Rate of the Reaction between Bromic, Hydriodic, and Arsenious Acids

For these experiments the reagents were mixed two by two—the arsenious acid and sulphuric acid solutions in one bottle and the potassium bromate and potassium iodide solutions in another. Both were kept in the thermostat, and for each experiment a certain amount of each was pipetted into a small stoppered bottle; the mixture was allowed to react for a measured time, and was then analyzed.

Before determining the iodine and arsenious acid in the product of the reaction, it is, of course, necessary to stop the reaction, or at least to slow it up so much that no appreciable change in the composition of the solution takes place during the progress of the analysis. In the present instance this is a difficult matter. Neutralization of the acid, or dilution of the solution, which stop or retard the liberation of iodine, accelerate its reaction with the arsenious acid; and it was only after many trials and calculations, based on the researches of Roebuck and of Clark, that the following method was perfected.

The mixture to be analyzed (75 cc in volume) was thrown into 450 cc of ice-cold water containing enough thiosulphate to remove all the iodine but one cubic centimeter (centi-normal) or less. The remaining iodine was titrated in two minutes with centi-normal thiosulphate and starch by daylight or by the light of an Auer mantle, but not by gaslight. Enough ammonium bicarbonate was added to make the solution alkaline, and finally the arsenious acid was estimated with iodine.

Under these conditions, and when the diluted mixture contains before titration 1 cc $n/100$ iodine, 25 cc $n/100$ arsenious acid, 15 cc $n/1$ sulphuric acid and 4 cc of F/1 potassium iodide, a correction of about 0.03 cc $n/100$ must be added to

the thiosulphate reading and to the iodine reading in the arsenite determination. This correction must be doubled if only half as much acid be present, and it varies roughly as the square of the excess of iodine not removed by the thiosulphate added to the water of dilution. If by mischance more thiosulphate has been added in dilution than is equivalent to the free iodine, this correction must not be applied.

If much bromic acid remains unreduced, iodine is liberated by it during the first titration. With the above mentioned concentrations of the various reagents, 25 cc $n/100$ bromic acid frees 0.02 cc $n/100$ iodine.

The error of the determinations is greater than the corrections, owing to the difficulty of making sure of the end-point with thiosulphate at such great dilution. This is the weakest point in the method of analysis adopted.

The results of three sets of experiments, with different concentrations of acid and iodide, are given in Tables VIII IX and X.

TABLE VIII

$KBrO_3$, 199; KI, 1984; H_2SO_4, 2000; As_2O_3, 200; Vol., 0.600 (75 cc titrated)

t	$x-y$ in 75 cc	As_2O_3-y in 75 cc	x	x calc.[1]	y	y calc.[2]	$K_1 \times 10^{15}$
6	4.60	24.78	4.82	4.63	0.22	0.23	1020
12	7.56	24.22	8.34	8.30	0.78	0.79	985
18	9.57	23.44	11.13	11.21	1.56	1.57	972
24	11.24	22.65	13.59	13.52	2.35	2.52	985
30	12.36	22.05	15.31	15.37	2.95	3.37	977
36	12.76	20.88	16.88	16.91	4.12	4.25	968
42	13.05	19.67	18.38	18.31	5.33	5.31	984

[1] Calculated by use of $K_1 = 980 \cdot 10^{-15}$ from Table I.

[2] K_2 varies with the concentration of the arsenious acid. Hence for the calculation of each number of the column, a value of K_2 corresponding to the same concentration of arsenious acid was chosen from Table IV, viz: 158 for the first three, 150 for $t = 30$, and 145 for $t = 36$ and $t = 42$.

TABLE IX

$KBrO_3$, 199; KI, 1980; H_2SO_4, 4000; As_2O_3, 200; Vol., 0.600 (75 cc titrated)

t	$x-y$ in 75 cc	As_2O_3-y in 75 cc	x	x calc.[1]	y	y calc.[2]	$K_1\times10^{15}$	$K_2\times10^{-4}$
3	7.28	24.83	7.45	7.43	0.17	0.10	828	—
6	11.74	24.67	12.07	12.22	0.33	0.32	797	—
9	14.92	24.48	15.44	15.68	0.52	0.68	789	—
12	17.00	24.01	17.99	18.15	0.99	1.06	793	—
15	18.38	23.57	19.81	19.93	1.43	1.50	796	—
18	19.21	23.16	21.05	21.06	1.84	1.98	783	—
21	20.20	22.57	22.63	22.18	2.43	2.45	—	—
24	20.40	22.04	23.36	22.88	2.96	2.95	—	—
70	16.52	16.77	—	—	8.23	—	—	—
80	15.77	15.90	—	—	9.10	—	—	—
90	15.25	15.27	—	—	9.73	—	—	137[3]
100	14.73	14.73	—	—	10.27	—	—	129
110	13.79	14.04	—	—	10.96	—	—	135

TABLE X

$KBrO_3$, 199; KI, 3968; H_2SO_4, 2000; As_2O_3, 200; Vol., 0.600 (75 cc titrated)

t	$x-y$ in 75 cc	As_2O_3-y in 75 cc	x	x calc.[4]	y	y calc.[5]	$K_1\times10^{15}$
5	7.04	24.96	7.08	6.84	0.04	0.06	—
10	11.58	24.83	11.75	11.52	0.17	0.22	935
15	14.52	24.62	14.90	14.88	0.38	0.43	909
20	16.68	24.25	17.43	17.33	0.75	0.70	917
25	18.13	23.98	19.15	19.24	1.02	0.99	901
30	19.13	23.58	20.55	20.52	1.42	1.31	911
35	19.80	23.28	21.52	21.53	1.72	1.63	906
40	20.09	22.96	22.13	22.30	2.04	2.01	—
						Average	911

The constant K_1, referring to the rate of reduction of the bromic acid (Equation 8), was calculated as described on page 298.

[1] $K'_1 = 810 \times 10^{-15}$ (Table II).

[2] Values of K'_2 from Table V.

[3] K'_2 calculated from $t = 70$ as initial point; see page 300.

[4] $K_1 = 909 \times 10^{-15}$, for Table III.

[5] $K_2 = 134 \times 10^4$, from Table VI.

The rate of oxidation of the arsenious acid by the iodine liberated during the reaction may be expressed by the equation

$$dy/dt = \frac{K_2(x-y)(As_2O_3-y)(Vol)^2}{(KI-x-y)^2(H_2SO_4-x-y)} \qquad (12)$$

and values of K_2 might be computed by substituting for x and y their "effective averages" and integrating as explained on page 298; the terms involving x and y being almost constant, there is no *petitio principii* in this procedure. It was thought better, however, to calculate y for each measurement of the table, using Equation 12 and the values of K_2 from Tables IV, V and VI. Similarly, the values of "*x calc*" are obtained by the use of K_1 of Tables I, II and III.

The calculated and observed values of x and of y are entered in adjoining columns in Tables VIII to X; the differences are sometimes positive and sometimes negative but in no case exceed the error of analysis; that is, the arsenious acid actually oxidized is just what was acted on by the iodine liberated during the reaction, none has been oxidized by the hypothetical primary products of the reduction of the bromic acid. If these intermediate products had been quantitatively reduced by the arsenious acid (as has been assumed in the case of the analogous reaction with hydrogen bromide) the arsenious acid oxidized would have been from three times to seventy times as much as that actually observed, while the iodine liberated would have fallen to zero.

Conclusions

In solutions containing bromic hydriodic and arsenious acids, no arsenic is oxidized except by the action of the iodine liberated during the reaction; and the rate of reduction of the bromic acid, and the rate of liberation of iodine are unaffected by the presence of arsenious acid, except in so far as the oxidation of the latter by the iodine affects the concentrations of acid and iodide in the solution.

The action of hydrogen iodide on bromic acid, therefore, does not "induce" the oxidation of arsenious acid; and there

is no ground for regarding the oxidation of arsenious acid in mixtures of bromic and hydrobromic acids as a case of chemical induction.

My thanks are due to Prof. W. Lash Miller at whose suggestion this investigation was undertaken and under whose direction it was carried out in the winter of 1905–6.

The University of Toronto,
February, 1907

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No. 66: THE COURSE OF THE OXIDATION OF β-NAPHTHOQUINONE TO PHTHALIC ACID, by MAITLAND C. BOSWELL.

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(On the Mechanism of the Oxidation of Naphthalene. II.)

THE COURSE OF THE OXIDATION OF β-NAPHTHOQUINONE TO PHTHALIC ACID

BY MAITLAND C. BOSWELL

In many of the reactions of organic chemistry, where the ultimate product is only distantly related to the substances initially present, it is of great interest to trace the intermediate steps of the reaction; either, for example, to elucidate some theory—as that of ring opening in the oxidation of cyclic compound—or in the hope of discovering constitutional formulas for, and ultimately achieving the synthesis of, the substances experimented on.

Up to the present, information as to the course of such reactions has been sought by examining the reaction products for the intermediate compound suspected; and by varying the conditions of the reaction, such as temperature and concentrations, by exchanging one oxidation or reduction agent for another, by adding alkali or acid, etc., to discover, if possible, conditions under which they would be formed in isolable quantities. Much has been accomplished in this manner.

There is, however, a second method of procedure which is illustrated by the experiments of the present paper; and which, so far as I am aware, has not hitherto been put in practice. This consists in studying the behavior of the suspected intermediate products with the reagents used in the reaction in question, in order to see whether, if formed, they would accumulate in the reaction mixture, or would be converted at once into the final product.

This second method is, in a sense, a complement of the first; each furnishes information that the other cannot give. Failure to isolate any particular substance cannot be regarded as proof that it did not exist temporarily at some stage of the reaction; and on the other hand, proof that the substance in question could not remain unaltered in the

presence of the reagents, is proof merely that it might have been—not that it actually was—formed as an intermediate stage of the reaction.

The first method, then, may lead to positive evidence that a given substance is one of the intermediate products of the reaction; the second, to positive evidence that it is not. Neither method can furnish evidence of the kind peculiar to the other.

A few simple experiments carried out by either of the two methods may often give valuable information; but to obtain really conclusive evidence by either of them, all the precautions suggested by the study of chemical kinetics must be observed. In applying the first method, in particular, it has too often been forgotten that change of conditions often entails a radical change in the mechanism of the reaction. An example of such a change is afforded by my experiments on the oxidation of β-naphthoquinone, discussed on page 127.

In a paper which has just been published, Mr. Daly[1] has made a careful study of some of the likely intermediate stages in the formation of phthalonic acid by the action of potassium permanganate on naphthalene. The present experiments with β-naphthoquinone and some of its possible oxidation products show how, under favorable circumstances, a few simple measurements may lead to equally definite results.

In the oxidation of β-naphthoquinone to phthalic acid,[2] the ring may be broken at the double bond, between the two keto groups, or between the CO and CH groups; of these, the last named seems the least likely, from chemical analogies, while simultaneous dissolution of two or more bonds is least likely of all.

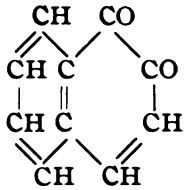
The first alternative would result in the formation of carboxy-phenylglyoxyl-formic acid, which on further oxidation might be converted into phthalonic acid and then into phthalic acid (Series *A*). The experiments of Zincke[3] and of

[1] Jour. Phys. Chem., 11, 93 (1907).

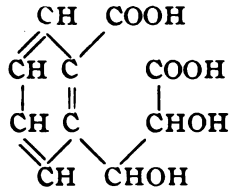
[2] Liebig's Ann., 189, 155 (1877).

[3] Ber. chem. Ges., Berlin, 25, 400 (1892).

Bamberger and Kitschelt,[1] who prepared ortho-carboxy-phenyl-glyceric acid by the action of chloride of lime on β-naphtho-



β-Naphthoquinone

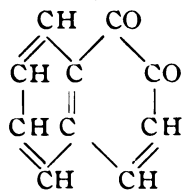


Ortho-carboxy-phenyl-glyceric acid

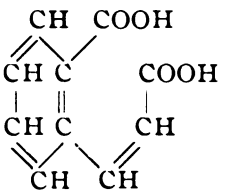
quinone, lend probability to the second supposition (Series *B*); and I have accordingly undertaken experiments to ascertain whether the oxidation by chromic acid follows the same course.

The first product of the oxidation, if the bond between the two keto groups be broken, would be *o*-carboxy-cinnamic acid. I do not find in the literature any account of this substance having been oxidized without loss of carbon, but cinnamic acid itself gives phenylglyceric acid;[2] *o*-carboxy-phenylglyceric acid may therefore be assumed, with perhaps *o*-carboxy-benzoylacetic acid (the hydrate of phthalyl-acetic acid) intermediate. Homophthalic acid, and carboxy-mandelic acid (the hydrate of phthalid-carbonic acid), both of which may be obtained from phthalonic acid by reduction, may also reasonably be regarded as possible stages in the oxidation, since my own experiments show that phthalonic acid is actually formed from each of them.

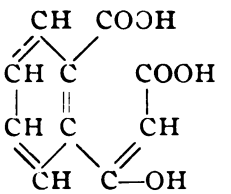
The steps by which β-naphthoquinone is oxidized to phthalic acid, on the assumption that the bond between the two CO groups is the first to break, may thus with some probability be assumed to be:



β-Naphthoquinone



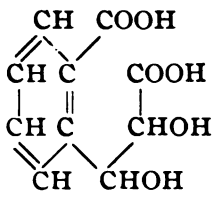
o-Carboxy-cinnamic acid



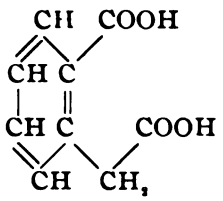
o-Carboxy-benzoyl-acetic acid

[1] Ber. chem. Ges., **25**, 888 (1892).

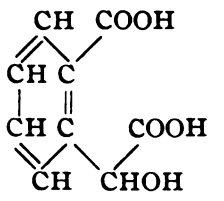
[2] Fittig: Liebig's Ann., **268**, 27 (1892).



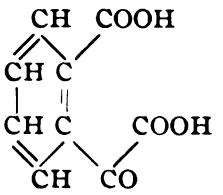
o-Carboxy-phenyl-glyceric acid



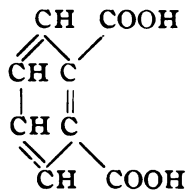
Homophthalic acid



o-Carboxy-mandelic acid



Phthalonic acid



Phthalic acid

Substances Used in the Experiments

β-Naphthoquinone, prepared by the method of Lagodzinski and Hardine[1] and purified by the method described in my paper on "Analytical Methods."[2]

The lactone of ortho-carboxy-phenylglyceric acid, by the method of Zincke;[3] melting-point 202°.

Ortho-carboxy-cinnamic acid, by the method of Ehrlich and Benedikt.[4]

Phthalyl-acetic acid, by the method of Gabriel and Neumann.[5]

Homophthalic acid, by the method of Graebe and Trümpy,[6] melting-point 174°–175°.

The lactone of phthalid-carbonic acid, by the method of Graebe and Trümpy,[7] melting-point 150°–152°.

Phthalonic acid, by the method of Graebe and Trümpy.[8] As I found that air-dried phthalonic acid does not contain a

[1] Ber. chem. Ges., Berlin, **27**, 3075 (1894).
[2] Jour. Am. Chem. Soc., **29**, 230 (1907).
[3] Ber. chem. Ges., Berlin, **25**, 405 (1892).
[4] Monatsheft, **9**, 528 (1888).
[5] Ber. chem. Ges., Berlin, **26**, 952 (1893).
[6] Ibid., **31**, 375 (1898).
[7] Ibid., **31**, 373 (1898).
[8] Ibid., **31**, 369 (1898).

definite amount of water of crystallization,[1] I used anhydrous acid which I prepared by heating the air-dried acid at 115° to constant weight.

α-Naphthoquinone, by the method of Japp and Miller,[2] and purified by repeated crystallization from petroleum ether; melting-point 124°–126°.

The α-naphthol and the naphthalene were "chemically pure" preparations of Kahlbaum.

Method of Working

The rates of oxidation were measured as follows: In a 150 cc glass stoppered bottle was placed 0.1000 gram naphthoquinone (or an amount of one of the other substances proportional to its formula weight); and a mixture of 70 cc of potassium bichromate solution (7.648 grams $K_2Cr_2O_7$ per liter) with 5 cc of dilute sulphuric acid (150 grams H_2SO_4 per liter) was added. The bottle was completely immersed in a bath of boiling water; at the expiration of a measured interval it was removed, emptied into a beaker containing 75 cc ice water and titrated with approximately fortieth-normal ferrous sulphate, using potassium ferricyanide as external indicator in the usual way. The results of the measurements are contained in Table I.

In the first column are the names of the substances; in the second the formulas; in the third the weights taken; in the fourth, after the duration of the oxidation in minutes, and after *Bi* the amount of bichromate reduced expressed in cc of a *solution* containing 7.648 grams $K_2Cr_2O_7$ per liter. In the fifth column, under *P*, are entered the number of cc of bichromate (calculated from the formulas) necessary to oxidize the substance to phthalonic acid, and under *T* the number of minutes (obtained graphically from the data of the table) in which these quantities of bichromate are reduced.

Of course, it cannot be assumed that at the moment *T* nothing but phthalonic acid is present in the solution, for that

[1] Jour. Am. Chem. Soc., 29, 230 (1907).

[2] Jour. Chem. Soc., 39, 220 (1881).

TABLE I

Substance	Formula	Weight taken Gram		Results of the Measurements							P	T
β-Naphtho-quinone	$C_{10}H_6O_2$	0.1000	t — 2.5	5	10	20	40	80	150	210		
			Bi — 4.4	14.4	21.6	27.3	31.6	37.7	41.5	45.7	40.5	128
Ortho-carboxy-cinnamic acid	$C_{10}H_8O_4$	0.1215	t — 30		60	90		120	150	180		
			Bi — 9.1		12.7	18.8		19.3	21.5	21.2	32.4	250
Ortho-carboxy-phenylglyceric acid	$C_{10}H_8O_5$ (Lactone)	0.1317	t — 30		60	90		120	150	180		
			Bi — 1.2		5.0	9.5		12.8	17.8	21.9	24.3	200
Phthalyl-acetic acid	$C_{10}H_6O_4$	0.1203	t — 30		60	90		120	150	200		
			Bi — 8.5		12.7	15.1		17.2	20.6	24.6	24.3	200
Homophthalic acid	$C_9H_8O_4$	0.1140	t — 30		90	120						over
			Bi — 0.5		1.2	1.9					16.2	1000
Phthalid-carbonic acid	$C_9H_6O_4$ (Lactone)	0.1130	t — 30		60	90		120				
			Bi — 1.5		3.6	5.1		6.9			8.1	160
Phthalonic acid (anhydrous)	$C_9H_6O_5$	0.1230	t — 40		80	140						
			Bi — 8.2		10.2	16.9					0	0
Phthalic acid	$C_8H_6O_4$	0.1050	t — 30		60	90						
			Bi — 1.0		3.0	6.0					—	—

substance itself is oxidized by chromic acid. This reaction, however, takes place slowly in the relatively dilute solution of chromic acid left by the previous oxidation, as is shown by the measurements of Table II.

TABLE II

Phthalonic acid Gram	Bichromate cc.	Sulphuric acid cc.	t. minutes	Bi. cc.
0.1230	70	5	40	8.2
0.1230	70	5	80	10.2
0.0615	70	5	40	2.7
0.0615	70	5	80	4.4
0.1230	35	5	40	6.0
0.1230	35	5	80	8.0
0.1230	70	2.5	40	6.3
0.1230	70	2.5	80	7.0

The weights of anhydrous phthalonic acid taken are entered under *Phthalonic acid*, the volumes of the bichromate solution and of the acid (page 123) under *Bichromate* and *Sulphuric acid* respectively, the duration of the oxidation under *t*, and the bichromate reduced under *Bi*. The great effect of the concentrations of the reagents on the rate is sufficiently obvious. From a graph of the results it appears that the rate is proportional to the concentrations of the sulphuric acid and of the bichromate respectively, and to the square of that of the phthalonic acid; but for the purposes of this paper it was not necessary to undertake special measurement to establish this relation rigorously.

Far the greater part of the phthalonic acid formed in my experiments would thus escape further oxidation; and, in fact, the presence of that substance in each of the solutions at the expiration of *t* minutes was established by the test with potassium permanganate described in my paper on "Analytical Methods."[1] This test was carried out as follows. First, the chromic acid remaining was reduced with ferrous sulphate. The phthalonic acid

[1] loc. cit.

was then isolated by neutralizing with sodium carbonate, acidifying with hydrochloric acid, evaporating to dryness on the water-bath, extracting with absolute alcohol and evaporating the alcoholic extract to dryness; the residue was then dissolved in a little water and filtered. The solution so obtained was acidified with dilute sulphuric acid, and decinormal permanganate was added; in every case the color was discharged, a reaction characteristic of phthalonic acid and serving to distinguish it from phthalic, homophthalic and phthalid-carbonic acids.

Phthalonic acid is thus an isolable product of the oxidation of all six substances studied; similar experiments showed that it is formed by the oxidation of α-naphthoquinone; hitherto it has been known as a product of oxidation of naphthalene[1] and of α-naphthol[2] only.

I

β-Naphthoquinone

A glance at Table I shows that the number entered under T opposite β-naphthoquinone is the smallest in the column. In other words, 0.1000 gram of the quinone is oxidized to phthalonic acid in less time than it would take to oxidize any of the hypothetical intermediate oxidation products of Series B (page 121), even if they had been present in full concentration and had the chromic acid all to themselves.

This shows conclusively that neither orthocarboxy-cinnamic, ortho-carboxy-phenylglyceric, phthalyl-acetic, homophthalic, nor phthalid-carbonic acid can be formed in the course of the oxidation of β-naphthoquinone to phthalic acid; and, as has been pointed out in the introduction, positive evidence of this nature can be obtained in no other way. That phthalonic acid is an intermediate product is shown by the permanganate test described above.

The measurements with *o*-carboxy-phenylglyceric acid

[1] Tscherniac: Ber. chem. Ges., Berlin, 31, 139 (1898); Graebe and Trümpy: Ibid., 31, 369 (1898).

[2] Henriques: Ibid., 21, 1607 (1888).

are particularly interesting, because the very preparation of this substance used in my measurements was itself made from β-naphthoquinone by the action of chloride of lime. There was therefore, *a priori*, a high degree of probability that it would prove to be one of the products of oxidation with chromic acid. Changing the oxidizing agent, however, has changed the whole course of the oxidation.

The experimental study of Series *A* was prevented by the circumstance that carboxy-phenylglyoxyl-formic acid has not yet been described in the literature, and that as yet I have had no leisure to attempt its preparation. In the present almost total absence of data of the kinetics of organic reactions, it is impossible to draw from its formula any sure conclusions as to its behavior on oxidation. The analogous phenylglyoxyl-formic acid, or rather an amino derivative of it, has been prepared by Baeyer and Homolka,[1] but nothing is said as to its behavior with oxidizing agents; similarly, nothing could be found as to the oxidation of dioxytartaric acid, or diphenyltriketone, both of which likewise contain the group CO.CO.CO. The result of my measurements, then, while conclusively disproving the possibility of the mechanism represented by the formulas of Series *B* leaves the question open as to Series *A*.

II

Genetic Relations between the Six Acids

From the data of Table I, collected in order to study the oxidation of β-naphthoquinone, some information as to the relations of the acids involved may be drawn. It is immediately obvious for instance, that homophthalic acid cannot be an intermediate product of the oxidation of either orthocarboxy-cinnamic, orthocarboxy-phenylglyceric, or phthalyl-acetic acids to phthalonic acid. Without further study of the relations between rates and concentrations, which (as aside from the main purpose of the research) was

[1] Ber. chem. Ges. Berlin, 16, 2219 (1883).

not undertaken, nothing further definite can be said; but if the plausible assumption be allowed, that in each case the rate is proportional to at least the first power of the concentration of the acids oxidized, then none of the acids studied can be considered as intermediate stages in the oxidation to phthalonic acid of those higher in the Table.

III

α-Naphthoquinone

In this connection, a few experiments were conducted with α-naphthoquinone, the results of which are given in Table III.

TABLE III

α-Quinone taken Gram	Results of the Measurements						P	T
0.1000	t — 30	60	90	120	150	180		
	B_1 — 5.1	11.6	20.8	26.2	31.6	35.6	40.5	220

Taken with the data of Table I these measurements show that orthocarboxy-cinnamic and homophthalic acids cannot be intermediate products in the oxidation of α-naphthoquinone to phthalonic acid under the circumstances of my experiments. Without further measurements to ascertain the effect of concentrations on the rates the same cannot be said of ortho-carboxy-phenylglyceric and phthalid-carbonic acids. Consideration of the structural formulas, however, makes it very unlikely. It is possible, however, to show from the data of Tables I and III that phthalyl-acetic acid cannot be an intermediate product.

40.5 cc bichromate are necessary to transform 0.1 gram of α-quinone into phthalonic acid and need 220 minutes to do it. 16.2 cc bichromate would be necessary to oxidize the quinone to phthalyl, acetic acid, and the table shows that this amount of bichromate is reduced in 77 minutes. Experiments on the rate of oxidation of phthalyl-acetic acid show (by interpolation) that in the last 22—077 = 143 minutes at most 0.51 equivalent[1]

[1] By one "equivalent" is to be understood the weight of substance entered in column 3 of Table I.

of that substance could be oxidized, leaving at least 0.49 equivalent that must have been oxidized in the first 77 minutes. This oxidation would require $0.49 \times 24.3 = 11.9$ cc of bichromate out of the 16.2 actually reduced, leaving only 4.3 reduced by the quinone. The phthalyl-acetic acid formed by the reduction of this amount of bichromate, however, amounts to only $4.3/16.2 = 0.26$ equivalent instead of the minimum of 0.49 required by the assumptions.

The assumption that phthalyl-acetic acid is an intermediate product of the oxidation of α-naphthoquinone to phthalonic acid is therefore disproved by the rate measurements.

The same process of reasoning makes it most improbable that phthalid-carbonic acid can be intermediate in the oxidation of orthocarboxy-cinnamic acid to phthalonic acid.

IV

α-Naphthol

The results of a series of experiments with α-naphthol given in Table IV show that homophthalic acid cannot be formed "on the way" to phthalonic acid; so far as my experiments go, however, any of the other six compounds studied may be intermediate compounds.

TABLE IV

α-Naphthol taken Gram	Results of the Measurements					P	T
0.091	*t*—30	60	90	150	180		
	Bi—18.6	20.1	25.1	26.7	29.2	56.7	580

V

The Action of Nitric Acid on Naphthalene

Laurent[1] and Beilstein[2] have shown that phthalic acid can be prepared by the action of nitric acid (sp. gr. 1.15) on naphthalene, and the latter even stated that "apart from the trouble of working in sealed tubes this is the cheapest way of

[1] Liebig's Ann., **19**, 38 (1836).

[2] Ibid., **202**, 215 (1880).

preparing this substance." I undertook a long series of measurements in the hope of ascertaining the mechanism of this reaction but without success, as in all my experiments—whether carried out in tubes or in open vessels—large quantities of nitro compounds were formed, and conditions could not be found under which oxidation took place anything like quantitatively.

The following table gives the results of a series of determinations of the phthalic acid produced by the action of 40 cc of nitric acid (sp. gr. 1.15) in six hours at 100° on naphthalene, α- and β-naphthoquinones, homophthalic, and phthalid-carbonic acids.

TABLE V

Substance	Weight taken	Phthalic acid formed
Naphthalene	2.0000	0.076
"	2.0000	0.074
α-naphthoquinone	0.0712	0.057
"	0.0712	0.045
β-naphthoquinone	0.0712	0.043
"	0.0712	0.038
Homophthalic acid	0.0814	0.036
"	0.0814	0.047
Phthalid-carbonic acid	0.0804	0.041
"	0.0804	0.041

SUMMARY

The method of determining the course of an organic reaction discussed in this paper is complementary to the method of isolation of intermediate compounds heretofore exclusively employed. It is shown that under favorable circumstances simple measurements may quickly lead to definite conclusions.

In the case of the oxidation of β-naphthoquinone to phthalic acid, phthalonic acid is an intermediate product, while *o*-carboxy-cinnamic, *o*-carboxy-phenylglyceric, phthalyl-acetic, homophthalic, and phthalid-carbonic acids are not.

Homophthalic acid is not an intermediate product in the oxidation of any of the other acids named, of α-naphthoquinone, or of α-naphthol.

o-Carboxy-cinnamic and phthalyl-acetic acids are not intermediate products in the oxidation of α-naphthoquinone.

These conclusions hold only for chromic acid as oxidizing agent; changing the oxidizing agent may change the whole course of the reaction.

My thanks are due to Prof. Lash Miller, at whose suggestion this research was undertaken.

The University of Toronto,
December, 1906

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No. 67: THE EXPERIMENTAL DATA OF THE QUANTITATIVE MEASUREMENTS OF ELECTROLYTIC MIGRATION, BY J. W. McBAIN.

(Communicated from Proceedings of the Washington Academy of Sciences, Vol. IX.)

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THE EXPERIMENTAL DATA OF THE QUANTITATIVE MEASUREMENTS OF ELECTROLYTIC MIGRATION.

TO THE END OF THE YEAR 1905.

COLLECTED AND ARRANGED BY JAMES W. McBAIN.

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INTRODUCTION.

THE following compilation is a result of a search through the literature of the subject in connection with my experimental work in 1904 at the University of Toronto on the transference numbers of the weak acids. So much time was required to find and collect the scattered papers in this field, that at the sugges-

tion of Professor W. Lash Miller I decided to compile a systematic summary of the existing data. I take this occasion of expressing to him my sincerest thanks for this suggestion, and for his valuable advice as to the arrangement of the results; and I desire also to acknowledge my indebtedness to the Carnegie Institution of Washington for the grant under which I was working.

The compilation was far advanced before I left Toronto, and the whole has been revised and brought up to date in Leipsic and Heidelberg. My thanks are due to Professor Luther for the interest he has displayed in the work, and to Professor Jahn for his kindness in furnishing me with out-of-print dissertations from his laboratory.

To make this collection has cost me many months of labor extended over the past three years; but any doubt of its usefulness is removed by the frequency with which I still chance on memoirs whose titles give no indication that they contain experiments on electrolytic migration.

PLAN OF THE BIBLIOGRAPHY.

My object is to present the results in tabular form, with enough of the experimental details to enable the reader to estimate the intrinsic value of the measurements. Hence in addition to the author, title, year, volume and page of the periodical in which the papers appeared, I have given in each case a full list of the chemicals experimented with, the concentrations of the solutions, the composition of the solvent, the nature of the electrodes, the amount of electrolysis (voltameter readings), the temperature, the change in the middle (supposedly unaltered) portions, the diaphragms employed if any, the number of experiments, and the final results; also some information as to the form and size of the apparatus, and occasional critical remarks.

The material is arranged chronologically[1]; an alphabetical index of authors, an index of chemicals, and an index to experiments made in solvents other than water, are provided. In the majority of cases, however, I have not stated the method of analysis employed, nor given the duration of the experiments (chance for diffusion).

[1] Alphabetically within the year.

EXPERIMENTAL METHODS.

The experimental methods of determining migration values are five in number: the analytical or Hittorf method (previously used by Faraday and by Daniell and Miller), the direct or meniscus-velocity method, the method based on measurement of concentration cells with and without diffusion, the method based on measurements of the limiting current density at which normal products occur at the electrodes, and the method of Nernst and Riesenfeld for two immiscible solvents with a linear distribution ratio (Verteilungscoefficient).

Of these only the first two as yet yield accurate and reliable results. The results of all five methods have been abstracted in the present bibliography.

The literature for the fourth method, mainly theoretical, is:

H. W. Weber, Wied. Ann., *7*, 469 and 536 (1879).

A. Witkowsky, ibid., *11*, 759 (1880).

C. L. Weber, Zeit. phys. Chem., *4*, 182 (1889).

Sheldon and Downing, Phys. Rev., *1*, 51 (1893).

B. Klössing, Beibl., *18*, 220 (1894).

Th. des Coudres, Wied. Ann., *57*, 232 (1896).

E. Salomon, Zeit. phys. Chem., *24*, 55 (1897); *25*, 336 (1898).

C. Ullmann, Zeit. f. Elektrochem., *3*, 516 (1897).

H. J. Sand, Phil. Mag. (6), *1*, 45 (1901); Zeit. phys. Chem., *35*, 641 (1901).

C. Christiansen, Drudes Ann., *8*, 787 (1902).

P. Straneo, Acc. dei Lincei (5), *11* (I), 58, 171 (1902).

F. G. Cottrell, Zeit. phys. Chem., *42*, 385 (1903).

U. Grassi, ibid., *44*, 360 (1903).

E. Brunner, ibid., *47*, 56 (1904).

ACCURACY OF THE DETERMINATIONS.

The accuracy of transport determinations is usually much overrated. For the better experiments of such workers as Bein, Kümmell, Loeb, and Nernst, and the best experiments of Hittorf, the results seem to be reliable to one or two units in the second decimal place; the work of Steele and Denison is more accurate. Very accurate measurements[1] have been made with

[1] Probably Tower's measurements of sulphuric acid fall in this class; the experimental details are inaccessible in Heidelberg.

four substances by Noyes and by Noyes and Sammet, and a long series has appeared from Jahn's laboratory, which are especially interesting as they are all made according to the same method; the analytical work is wonderful. Noyes has more confidence in the absolute value of his results than Jahn has in his, although the experiments of Noyes and Sammet hardly surpass the best work of Jahn's pupils. However I have copied the results of Noyes to four decimal places, while Jahn calculates his to three.

Luther[1] estimates the reliability of the best measurements as amounting to one or two units in the third decimal place; and E. Wolff,[2] one of Jahn's pupils, speaks of the "hitherto accepted limit of accuracy of one per cent." It seems much easier to obtain constant results than absolutely reliable values; the difference between the final values of two investigators is often several times as great as the maximum difference between the individual results of either.

ERRORS INTRODUCED BY THE USE OF DIAPHRAGMS.

Even in the earliest experiments the difficulty of preventing the mixing of the solutions through convection currents was met by the use of diaphragms. Faraday used a porous asbestos wick, Daniell and Miller porous earthenware, while Hittorf employed intestinal membrane in most of his measurements.

Recently Bein[3] and then Hittorf[4] investigated the influence of various membranes upon the migration values, and found that while some of them, such as earthenware, had no influence apart from cataphoresis, others changed the migration values of many substances very greatly. Nernst attempted[5] to deal with these cases by his theory of the phenomenon at the meniscus between two immiscible solvents during electrolysis, and Hittorf[6] replied; it seems to me that the objections raised by the

[1] Winkelmann's Handbuch der Physik, 2 Aufl., 1905, Bd. IV, 868. This excellent review of the subject contains also a selection of the most accurate work up to 1903, including experimental details.

[2] Dissertation, Berlin, 1903.

[3] Zeit. phys. Chem., *28*, 439 (1899).

[4] Arch. neer. (2), *6*, 671 (1901); Zeit. phys. Chem., *39*, 613 (1902); *43*, 239 (1903); Zeit. f. Elektrochem., *8*, 481 (1902).

[5] Drude's Ann., *8*, 600, 609 (1902); Zeit. f. Elektrochem., *7*, 644 (1902).

[6] Drude's Ann., *9*, 243 (1902).

latter might be removed by assuming the existence of hydrated ions.

In general it is possible to obtain good results without casting suspicion upon them by the use of membranes, as is shown by the accurate measurements of Noyes and Sammet, Jahn's pupils and others. For measuring very weak electrolytes such as acetic acid, the use of some sort of diaphragm is almost indispensable; I used bundles of glass tubes of small bore, which is cumbersome, but is otherwise free from criticism. The diaphragms which are least open to objection are cloth, cotton batting, earthenware, and agar-agar. It is unfortunate that it is just in the case of weak electrolytes where diaphragms would be most useful that cataphoresis (electric endosmosis) is most prominent. Solidified gelatine, intestinal membrane, fish-bladder, gold-beaters' skin, membrane of an egg, and parchment, are the diaphragms which exert the greatest influence upon the migration; the influence varies with the nature of the electrolyte and its concentration.

ERRORS INTRODUCED BY THE METHOD OF CALCULATION.

There are several methods of calculation in use, although only one of them is correct. Hittorf described this with the greatest clearness in his classical researches; yet of only sixteen authors besides Jahn's pupils can I say with certainty that their results were correctly calculated. In many cases the data given in the papers are not sufficient to warrant a definite expression of opinion; but it is safe to assert that of the authors who used the analytical method, not more than half calculated their results correctly.

In measuring migration we are measuring the movement of the electrolyte through the solvent; hence the calculation must be based upon a constant amount of solvent. If for example we find that before electrolysis the m grams of water in an electrode compartment contains a certain amount of electrolyte, we must determine the amount of electrolyte contained in m grams of water after electrolysis. The favorite among the other methods is to determine the amount of electrolyte in a constant volume of solution before and after electrolysis; it is evident that only

in special cases will equal volumes of solutions of different concentrations contain the same amount of solvent. Hittorf[1] picked out particular cases measured by Wiedemann and showed that the error thus introduced amounted to as much as 20 percent of the migration value; in other cases it was negligible. In very dilute solutions this error vanishes. Another method bases the calculation upon constant weight of solution; as is evident, this is always wrong. Here, again, the error is worst in concentrated solutions, and becomes negligible when the solutions are very dilute. In general, I have had to leave it to the reader to calculate whether the error introduced by wrong methods of calculation is large or not; in a few cases, however, I have made the calculation myself, and when the error was vanishingly small, I have stated that the results were correctly calculated.

Possibly the following consideration of the effect on the transport number caused by neglecting the loss of gases at the electrodes may be of use. During the passage of 96,540 coulombs 8 grams of oxygen escape, hence the amount of the constituents of the solvent at the anode appears to be 8 grams less than really was, and so the apparent migration value of the anion is increased by the number of g-mols of electrolyte contained in 8 grams of water. This holds for all electrolytes where oxygen is evolved at the anode. Similarly, the migration value of the cation obtained at the cathode where hydrogen is escaping is increased by the number of g-mols of electrolyte in one gram of water; this is generally negligible. The correction to be subtracted from the migration value of the anion found by analysis at the anode is therefore 0.008 for normal solutions and 0.0008 for decinormal solutions; similarly for the cathode analysis, one eighth as much has to be added to the migration number of the anion. These corrections are mostly negligible, but the calculation is useful as showing the absolute value of the errors introduced by the chemical processes at the electrodes. It is easy to extend it to other cases; for instance, the correction at the cathode where a metal is precipitated and not weighed, is equal to its gram-equivalent weight multiplied by the correction de-

[1] Pog. Ann., *103*, 8 (1858).

duced above for hydrogen. For a metal dissolving at the anode, where the electrode is not weighed, the correction is equal to the correction for oxygen (but taken with opposite sign) multiplied by one-eighth the gram-equivalent weight.

INTERPRETATION OF THE RESULTS.

The transport number of any component of a solution is the number of gram-equivalents of that component which enters or leaves one of the electrode compartments during the passage of 96,540 coulombs of electricity.

Hittorf has shown how in certain cases (double cyanides, stannic chloride, cadmium iodide, for instance) these transport numbers may suggest definite views as to the constitution of the electrolyte. In the following paragraphs I shall briefly discuss the bearing of transport measurements on the hypothesis of hydrated ions, and on that of the possible movement of undissociated molecules of the electrolyte; and I shall explain the methods of calculating the concentrations and mobilities of the complex ions or products of hydrolysis that may be assumed to exist in the solutions of certain salts. A few measurements which are not easily reconcilable with the prevalent theory of solutions are collected under the heading "anomalous results."

Hydrated Ions.

In a solution of sodium chloride (to take a concrete example) it is customary to assume the ions $Na^{\cdot}$ and Cl' together with water and undissociated molecules of NaCl. It is, however, possible to assume the existence of hydrated ions: $(Na+xH_2O)^{\cdot}$, and $(Cl + yH_2O)'$, or of complex ions, or even that the undissociated NaCl moves towards one of the electrodes, under the influence of a fall of potential, as colloids do.

If hydrated ions be assumed, it is evident that in calculating the transport numbers from the experimental data, allowance must be made for the water carried by them into the electrode compartments and set free at the electrodes. I have shown elsewhere[1] that this correction may be expressed by the formula $\left(\frac{l_A}{A}y - \frac{l_K}{A}x\right)C$, in which l_K and l_A represent the mobilities of

[1] Zeit. f. Elektrochemie, *11*, 216 (1905).

the cation and anion respectively, x and y the number of g-mols of water combined with one equivalent of each ion, Λ the equivalent conductivity, and C the total concentration of the electrolyte expressed as the number of g-equivs solute in one g-mol water. Thus it is evident that if the transport numbers of the hydrated ions are to be very different from those of $Na^{\cdot}$ and Cl', either the ions must differ widely in mobility and have a large amount of combined water, or the difference in hydration of the ions must be great. The numerical example given in the paper quoted shows that in general the change in the transport number caused by assuming that the ions are hydrated, is small. In very concentrated solutions, however, the difference would be greater; and the hypothesis might be checked by measuring the transport of some non-electrolyte added to the solution, choosing one which will not react with the electrolyte in question.[1]

Movement of Undissociated Electrolyte.

The fact that transport numbers for simple electrolytes are independent of the concentration discredits the hypothesis. The movement of non-electrolytes measured by Nernst, Garrard and Opperman[2] and by Morgan and Kanolt[3] corresponds to a transport number of the order of magnitude of 0.01. This is however a negligible quantity, being within the experimental error of most measurements; and the alternative assumption of hydrated ions is from other considerations very plausible.[4]

Complex Ions, Hydrolysis.

Three methods have been worked out for dealing with electrolytic solutions which are assumed to contain complex ions in equilibrium with simpler ions and undissociated molecules; the first was developed and applied by Burgess and Chapman, the other two by myself. The first and second methods are applicable to special cases only; the third is general, and may also be employed in dealing with hydrolysis.

(i) The method of Burgess and Chapman[5] is based on the

[1] Ibid., *11*, 961 (1905).
[2] Nachr. Gött. Akad., 1900, 68.
[3] Zeit. phys. Chem., *48*, 365 (1904).
[4] See Baur, Ahren's Sammlung, *8* (1903).
[5] Jour. Chem. Soc., *85*, 1305 (1904).

results of the careful study that has been devoted to solutions of iodine in potassium iodide solutions. Jakowkin and others have shown by means of several physico-chemical methods that KI_3 and KI are electrolytes of equal degree of dissociation; the dissociation constant for the reaction $\bar{I}_3 \rightleftharpoons I_2 + \bar{I}$ is also known, from these data and a transport determination in solutions containing iodine and potassium iodide the mobility of the tri-iodion was calculated, and found to agree with that calculated from conductivity measurements assuming that the dissociation of potassium tri-iodide is the same as that of potassium iodide.

(ii) In solutions of the haloid salts of cadmium and zinc the transport of the halogen increases rapidly with the concentration, and finally approaches a maximum. This may be interpreted by assuming that, when the maximum is reached, the concentration of the simple ions is negligibly small; by making suitable assumptions as to the formula of the complex its transport number may be calculated, and from the experimental numbers for intermediate concentrations the relative amounts of simple and complex ion may be obtained.

In the case of cadmium iodide[1] the numbers so arrived at are in accord with freezing point, and conductivity, and with the requirements of the mass law. The applicability of the method is restricted by the condition that, if the results are to be reliable, the maximum must be reached before the solution becomes too concentrated.

(iii) The third method is based on the assumption that in solutions containing a number of ions the migration of each is given by the product of its concentration into its migration velocity. This view was advanced by Hittorf in 1857; it has been tested and confirmed by numerous experimenters with known mixtures of two simple salts having a common ion; and it has been used in the mathematical developments of Kohlrausch.[2]

Let u, v, w, x, represent the mobilities of the ions $K^{\cdot}$, $Cd^{\cdot\cdot}$,

[1] R. Schrader, Zeit. f. Elektrochem., *3*, 498 (1897). E. v. Stackelberg, Zeit. phys. Chem., *23*, 493 (1897). K. Hopfgartner., Zeit. phys. Chem., *25*, 115 (1898). H. Jahn, Zeit. phys. Chem., *27*, 354 (1898). H. Hoffmeister, Zeit. phys. Chem., *27*, 345 (1898). E. Berliner, Dissertation, Berlin, 1902 — to appear this Winter with other work from Jahn's laboratory in the Zeit. phys. Chem.

[2] Wied. Ann., *62*, 209 (1897).

I', and CdI_3' respectively, in a solution of potassium cadmium iodide; and a, b, c, d, their concentrations expressed as gram-equivalents per cubic centimeter. Three of the mobilities, viz.: u, v, w, may be taken as known; and among the four concentrations there must exist the relation

$$a + b = c + d$$

so that four of the eight symbols, u, v, w, x, a, b, c, d, represent unknowns. Four experiments giving four independent relations involving these four are therefore necessary in order to determine the concentration of each of the ions, and the mobility of CdI_3'. Such, for example, are the following:

1. The specific conductivity x may be determined; by Kohlrausch's law

$$au + bv + cw + dx = x.$$

2. The quantity of potassium which enters the cathode compartment during the passage of one faraday through the solution may be determined; it is au/x equivalents.

3. Similarly, the net gain of cadmium in the anode compartment per faraday, is $(2dx - bv)/x$ equivalents.

4. And the gain of iodine at the anode per faraday: $(cw + 3dx)/x$ equivalents.

These are not the only experiments, however, that might be employed. By means of E.M.F. measurements, for instance, the concentrations b or c might be determined; the freezing point gives $a + \frac{1}{2}b + c + d$, etc. The experiments thus furnish more equations than unknowns, and the surplus may be used to check the theory. This has been done in my paper[1] in which the concentrations were calculated from transport measurements and one E.M.F. determination; the results so obtained are in accordance with the conductivity and freezing points.

It may be remarked that when the number of analytical components among the ions of a solution is represented by n, the migration of the n-th may be calculated from those of the remaining $n - 1$ by means of the stoechiometrical relations. Hence agreement between the directly measured migration of the n-th component and the calculated value is the best proof that unsuspected ions (due to hydrolysis, for example) have not been overlooked.

[1] Zeit. f. Elektrochem., *11*, 961 (1905).

Anomalous Results.

Of remarkable results there are many. Highly interesting are the researches of Daniell and Miller in 1844. These well known and capable experimenters, fully alive to the significance of the results they were obtaining, found that in many cases components now recognized as cations did not move at all. Later measurements agree in showing that in these very solutions the cation moves about as fast as the anion. Hittorf and others have suggested explanations for Daniell and Miller's results, but unfortunately the explanations suggested only make things worse.

Chassy, in 1890, made a number of measurements with mixtures of two and more electrolytes. His results are summarized by Ponsot[1] and are quite at variance with the predictions of the present theory; his is the only experimental work in this field.

Bein, in 1898, found for ammonium hydroxide a transport number widely different from that predicted by Kohlrausch's law of the independent migration of the ions. In 1904 I obtained a similar result for acetic and propionic acids. These are the only measurements that have been made with very weak electrolytes, and all three obey Ostwald's law; these results should not be so difficult to believe when Jahn and Nernst hold that the mobility of an ion varies greatly with the concentration, without any more evidence than that the conductivity and freezing points which agree so well with one another both refuse to obey Ostwald's law, although the latter does not take into account the possible displacement of the equilibrium by the electrical forces.

The accurate measurements of Noyes and Sammet in 1902 gave a result for hydrochloric acid differing by four percent from that calculated from the careful conductivity measurements of Goodwin and Haskell;[2] the transference measurements have been confirmed in Jahn's laboratory by Joachim, and the divergence has to be regarded as real. Divergences equally great even amongst the most carefully measured electrolytes are so

[1] Comptes rendus, *138*, 192.

[2] Phys. Review, *19*, 369 (1904).

common, that Luther has come to the conclusion that it is not worth while discussing whether Kohlrausch's Law is strictly quantitative or not until the experimental data are more reliable.

QUALITATIVE EXPERIMENTS.

Qualitative or semi-quantitative experiments are sufficient to show whether a given component of a solution moves toward the anode or toward the cathode during electrolysis. In order that the results may be decisive as to the constitution of the solution, however, further experiments must be made to find whether or no the component in question is present in colloidal form; this has been done in recent papers from the Leipsic laboratory.

If the experiment is carried out by electrolysing the solution between two other "electrode solutions," the presence of one of the components of the intermediate solution in the cathode compartment may justly be regarded as evidence that the component in question formed a constituent of some cation; the converse, however, is not necessarily true. It is possible that the component which in the intermediate solution formed part of a cation might have acted as anion in the cathode solution, and that it was consequently, in large part at least, driven out as soon as it entered. The experiments of Richards and Bonnet in 1904, and of Lind in 1903, offer a case in point; the authors are however doubtless justified in the conclusions which they draw, for the rate of transformation of the various modifications of chromic sulphate into each other is notoriously slow.

ARRANGEMENT OF THE ABSTRACTS, ABBREVIATIONS USED.

In the following abstracts general information is given in a paragraph which does not require further explanation. In the tables, the first column gives the chemical measured; the second the concentration (m denotes mols, that is gram-formula-weights); the third the temperature; the fourth the number of grams of silver or copper deposited in the voltameter, indicated by the abbreviation "g Ag," "g Cu," etc.; the fifth the per-cent change in the composition of the middle (supposedly unaltered) portions, calculated by myself; the sixth, the number of experiments ("ex"); the next indicates which electrode solution

was analyzed, "a" denoting the anode compartment, "c" the cathode compartment, and "ac" meaning that both were analyzed and used in computing the transport number; next comes the transport number of the anion, here the cipher before the decimal point is always omitted, and the number is filled out to three decimal places by dashes when the experiments were less accurate; attached to the transport number is given half the maximum divergence (multiplied by 1,000) between the individual results, preceded by the sign ±.

Thus "23 ex a .170 ± 4" means that 23 experiments were performed, the analyses at the anode compartment were used to compute the transport, the transport number found for the anion was 0.170, the maximum divergence between the individual results was 0.008. Very inaccurate experiments would be given as follows: "5 ex ac .51 — ± 67" meaning that the transport number found is 0.51, and the difference between the two extreme results was 0.134. Noyes' results are given thus: "ac .1657 ± 2.3" meaning 0.1657 with a maximum difference between the results of 0.0046. I am convinced that this maximum divergence does not in most cases give an exaggerated impression of the inaccuracy of the experiments.

The arrangement just described is followed as far as possible; often, however, a column is left out when the data are lacking, or when they have been given in the paragraph at the top. Extra columns, special arrangements of the data, etc., are explained in each special case.

In deciding what experiments it was fair to average together, in almost all cases I have been much more tender with the results than the authors themselves; many authors show what they think of their own results by averaging together all their values, even when obtained under different conditions of temperature and concentration. When only one experiment was performed under each set of experimental conditions, I did not feel justified in averaging the results even where their accuracy seemed questionable. Thus I have tried to give the experiments the benefit of the doubt; the reader should take this into account when trying to decide in any particular case whether the transport numbers really vary with the temperature, etc., or not.

ABSTRACT OF THE LITERATURE OF ELECTROLYTIC MIGRATION.

1814. R. Porrett.

Abstracts Phil. Trans., *1*, 510, from Phil. Trans., p. 519. On the Nature of the Salts termed Triple Prussiates, and on Acids formed by the Union of certain Bodies with the Elements of Prussic Acid.

The author observed the movement of Fe and of K in the electrolysis of ferrocyanic acid solution.

1833. M. Faraday.

Experimental Researches in Electricity, fifth series, III, Theory of Electrochemical Decomposition. Phil. Trans., *123*, 682, 525–530. Ostwald's Klassiker, *86*, 85. Pogg. Ann., *32*, 436.

Two pieces of apparatus, each consisting of two electrode cups connected by a strip of asbestos, were set up in series. One was filled with sulphuric acid of specific gravity 1.0212, the other with a chemically equivalent solution of sodium sulphate. Pt electrodes were used and the contents of the four cups were weighed and titrated before and after the electrolysis. The change in acidity in each cup of the sodium sulphate apparatus was $2\frac{1}{2}$–3 times as great as in the sulphuric acid apparatus. The sulphuric acid contained a small percentage of inorganic sulphates. (From these experiments it would follow that in sulphuric acid n for SO_4 lies between .4 and .33.)

1839. J. F. Daniell.

On the Electrolysis of Secondary Compounds. In a letter addressed to M. Faraday. Phil. Trans., *129*, 97.

Apparatus: A vertical U-tube with two diaphragms of bladder in the bend; tubes were attached to collect the gases from each of the electrodes separately. The current was measured by a water voltameter. In seven electrolyses with 1–10 percent solutions of sulphuric acid the migration value of the SO_4 was found to be $n = \frac{1}{4}$. In one of these experiments a Zn anode was employed, in the others Pt electrodes were used. As a result of futher electrolyses, the author concluded that the current was carried solely by the electrolyte, and adopted Davy's formulas for the oxy-acids and their salts, and those of Berzelius for the ammonium salts.

1840. J. F. Daniell.

Second letter on the Electrolysis of Secondary Compounds. Addressed to M. Faraday. Phil. Trans., *130*, 209.

The author electrolyzed various solutions in an apparatus consisting of two electrode compartments connected to a third cell by a siphon with partitions of membrane. The total electrolysis was determined by measuring the gases evolved. The solutions in each of the three cells were analyzed. In the experiments with caustic alkalis the membranes were replaced by porous earthenware.

H_2SO_4	specific gravity 1.076	$n = \frac{1}{4}$
H_3PO_4	6–11 percent	$n = \frac{1}{4}$
KOH		$n = \frac{1}{4}$
$Ba(OH)_2$	specific gravity 1.0085	$n = \frac{1}{3}$
$Sr(OH)_2$	specific gravity 1.007	$n = \frac{1}{3}$
K_2SO_4		$n = \frac{1}{4}$

1844. J. F. Daniell and W. A. Miller.

Additional Researches on the Electrolysis of Secondary Compounds. Phil. Trans., *134*, 1; Pogg. Ann., *64*, 18.

Apparatus: a horizontal cylinder divided into three compartments by vertical partitions of bladder. The Pt electrodes were placed in the end compartments which were provided with tubes for collecting the gases evolved. A water voltameter was placed in the circuit.

Experiments with copper sulphate, zinc sulphate, and ammonium chloride showed that the cation was not moved by the current. For potassium sulphate, barium nitrate, and calcium sulphate, the migration values were respectively $n = \frac{2}{3}$, $n = \frac{5}{6}$, $n = 1\frac{1}{2}$. Semi-quantitative experiments showed that both ions were moved in the cases of sodium tungstate, potassium chromate, potassium arsenite, and sodium carbonate; in the case of sodium chloride the chlorine was moved in greater amount than the sodium.

Further experiments were carried out with copper sulphate, aluminium sulphate, ferric sulphate, magnesium potassium sulphate, potassium aluminium alum, potassium copper sulphate, potassium sulphocyanide, potassium cyanide, potassium ferrocyanide, potassium ferricyanide, potassium sulphate, ammonium oxalate, potassium arsenite, potassium arseniate, sodium sulphite, sodium hyposulphite, and the phosphates of sodium.

1845. M. Pouillet.

Note sur l'electrochimie. Comptes rendus, *20*, 1 sem., 1544.

Apparatus: a U-tube; capacity 10 c.c.; Pt electrodes; no diaphragms; no middle portion; a water voltameter.

The author found no transport of gold in solutions of gold chloride; for the chlorides of iron, manganese, and cobalt $n = .66 -$; for other chlorides n lay between .7 — and .8 —. The author deduced that the action of the electrodes is unequal owing to the positive and negative constituents of an electrolyte having electric charges opposite in sign but unequal in amount.

1853. W. Hittorf.

Ueber die Wanderungen der Jonen während der Elektrolyse. Pogg. Ann., *89*, 177, Ostwald's Klassiker, *21*.

Apparatus: (i) a short wide glass cylinder of which the two parts could be isolated by sliding the upper half sideways; capacity 44 c.c.; the anode consisted of the metal corresponding to the electrolyte; the cathode was of Ag. No middle portion; no diaphragms. In the second column are given the number of grams of water in which one gram of salt was dissolved.

$CuSO_4$	6.35	5°	1g Ag	i	1ex	c.724
	9.56	5°	1	i	3	c.712
	18.1	4°	0.9	i	1	c.675
	40–148	4°	0.5	i	3	c.644
	9.56	20°	1.4	i	1	c.713
$AgNO_3$	2.48	11°	1.2g Ag	i	1ex	c.468
	2.73	19°	1.9	i	1	c.478
	5.18	18°	1.1	i	1	c.495
	10.4	19°	0.5	i	1	c.51 —
	14–247	19°	0.2	i	5	c.526
Ag_2SO_4	123	17°	0.1g Ag	i	3ex	c.554
$AgC_2H_3O_2$	127	15°	0.2g Ag	i	3ex	c.373
$AgNO_3$	30.9	4°	0.2g Ag	i	2ex	c.573 in ethyl alcohol.

1856. W. Hittorf.

Ueber die Wanderungen der Jonen während der Elektrolyse. Pogg. Ann., *98*, 1, Ostwald's Klassiker, *21*.

Apparatus: (ii) Cathode cylinder fitted into neck of anode cylinder; capacity about 80 c.c.; Ag cathode; no middle portion; no diaphragms. (iii) Horizontal cylinder divided by two partitions of porous earthenware into three compartments. (iv) Four superposed glasses, with diaphragm of intestinal membrane (Darmhaut); the upper (cathode) vessel contained free

acid; the middle portion was tested for acid and cadmium. This apparatus (iv) was made in four sizes for solutions of different concentrations; the smallest anode vessel contained 12 c.c., the largest 238 c.c.; Pt cathode, Cd anode.

In the second column are given the number of g water in which one g of salt are dissolved.

$CuSO_4$	9.56		0.8g Ag	ii	1ex	a.716	Cu anode.
	11.6		2.0	iii	2	a.704	" "
KCl	4.85	12°	1.1g Ag	iv	1ex	a.516	
	6.61	4°	0.7	iv	2	a.516	
	18.4	7°	0.8	iv	1	a.514	
	39.4	9°	0.7	iv	2	a.515	
	254	50°	0.6	iv	2	a.515	
	449	90°	0.4	iv	1	a.503	
KBr	2.36	12°	0.7g Ag	iv	2ex	a.528	
	117	7°	0.7	iv	2	a.513	
KI	2.7–8.5	1–12°	0.8g Ag	iv	3ex	a.511	
	170.3	3°	0.4	iv	1	a.492	
K_2SO_4	12	4–12°	0.9g Ag	iv	2ex	a.500	
	413	7°	0.3	iv	2	a.498	
KNO_3	5.8	9°	0.4g Ag	iv	2ex	a.450	
$KC_2H_3O_2$	1.4–48	14°	0.7g Ag	iv	2ex	a.335	
NH_4Cl	5.28	12°	1.1g Ag	iv	1ex	a.517	
	12.2	10°	1.5	iv	1	a.514	
	28.0	10°	0.9	iv	1	a.514	
	175	7°	0.7	iv	1	a.508	

1856. G. Wiedemann.

Ueber die Bewegung der Flüssigkeiten im Kreise der geschlossenen galvanischen Säule und ihre Beziehungen zur Elektrolyse. Pogg. Ann., *99*, 177.

Apparatus: two glass jars connected by a wavy siphon, capacity 200 c.c.; Pt electrodes; no diaphragms; no middle portion. Blank experiments showed the existence of an unchanged middle portion in the cases of sodium sulphate and potassium iodide.

Hittorf, Pogg. Ann., *103*, 8, shows that the results are incorrectly calculated. In the electrolyses of the copper salts between Pt electrodes, the acid formed at the anode reached the cathode portion, and Wiedemann points out that the current was partly carried by free acid.

A further series of determinations were made using porous earthenware diaphragms, repeating the experiments with sul-

phuric acid, nitric acid, copper sulphate, copper nitrate and silver nitrate. The results when corrected for cataphoresis corresponded with the numbers obtained with the apparatus described above in which diaphragms were avoided.

The concentrations are indicated in the second column in grams of SO_4, NO_3, etc., per 100 c.c.

H_2SO_4	2–14 SO_4	1.3–2.4g Cu	3ex	ac.180 ± 6	
HNO_3	7.7 NO_3	2.0g Cu	1ex	a.148	
	4.2 NO_3	2.0	1	a.142	
KOH	2.23 K	0.6g Cu	1ex	ac.245	
	2.09 K	0.6	1	ac.215	
NaOH	3.13 Na	1.1g Cu	1ex	ac.161	
	2.63 Na	1.1	1	ac.153	
$CuSO_4$	3.67 Cu	1.4g Cu	1ex	ac.181	
	1.52 Cu	0.7	1	ac.186	
	3.17 Cu	0.5	1	ac.360	Copper anode.
	2.54 Cu	0.5	1	ac.355	" "
	1.78 Cu	0.3	1	ac.321	" "
	1.52 Cu	0.3	1	ac.339	" "
$Cu(NO_3)_2$	1.66 Cu	0.9g Cu	1ex	ac.241	
	2.72 Cu	0.9	1	ac.368	Copper anode.
$AgNO_3$	1.92 Ag	1.3g Ag	1ex	ac.236	
	2.96 Ag	1.6	1	ac.535	Silver anode.
	2.66 Ag	1.0	1	ac.521	" "
NaCl	1.94 Na	0.6g Cu	1ex	ac.378	

1857. A. Weiske.

Die Ueberführung des Chlors bei der Elektrolyse seiner Verbindungen mit den Metallen der Alkalien und alkalischen Erden. Pogg. Ann., *103*, 466, Habilitations Dissert.

Apparatus: two flasks connected by a straight tube with a glass cap; capacity 100 c.c.; no diaphragms; no middle portion.

The calculation is based (incorrectly) upon constant volume of solution.

The author discusses the prevalent theories of electrolysis.

KCl	1–10	percent	0.4g Ag	10ex	c.516 ± 9
NaCl	9.21	percent	0.4g Ag	4ex	c.686 ± 8
	2.86	"	0.4	4	c.685 ± 9
	0.844	"	0.2	1	c.680
$CaCl_2$	1–9	percent	0.3g Ag	9ex	c.690 ± 8
$BaCl_2$	0.5–8	percent	0.3g Ag	8ex	c.531 ± 9
$SrCl_2$	1.07	percent	0.3g Ag	4ex	c.648 ± 8
	0.757	"	0.3	3	c.650 ± 9
	0.146	"	0.2	1	c.655

1858. W. Hittorf.

Pogg. Ann., *103*, 1; Ostwald's Klassiker, *21*.

Apparatus: (iv) see Hittorf, 1856. In these experiments a Zn anode was used and the cathode was surrounded by a solution of potassium chloride; (v) four superposed glasses of which the uppermost contained the anode and the lowest the cathode. The cathode was bent into the form of a U-tube to permit the escape of hydrogen. Earthenware and bladder diaphragms.

In the second column are given the number of grams of water in which one gram of salt was dissolved.

KCl	5.2–5.6		1.0g Ag	iv	6ex	a.513
	98		1.0g	iv	8	a.509
	3.8–5.5		0.5	v	2	c.501
KNO_3	4.62	12°	0.6g Ag	v	1ex	c.479
	9.63	11°	0.8	v	1	c.487
	31.5	7°	0.4	v	1	c.494
	94.1	8°	0.7	v	1	c.497
$KC_2H_3O_2$	1.3–94	14°	0.8g Ag	v	3ex	c.331

In addition experiments are detailed showing that in solutions containing potassium iodide and potassium chloride both I and Cl are transported by the current.

1859. W. Hittorf.

Pogg. Ann., *106*, 337, 513. Ostwald's Klassiker, *23*.

Apparatus: (ii) See Hittorf, 1856. (iv) See Hittorf, 1856, for the experiments with potassium cyanide the membranes were replaced by porous earthenware; in the experiments with the alkaloid hydrochlorides the cathode was surrounded by hydrochloric acid. (v) See Hittorf, 1858. (vi) Five superposed glasses with membranes. Anode of Cd in the lowest vessel, Pt cathode in the uppermost. The anode was surrounded with a protecting solution: potassium acetate in the experiments with potassium oxalate, potassium chloride in those with potassium chromate, sodium chloride in those with sodium mono- and di-sodium phosphates, sodium nitrate in those with sodium phosphate and pyrophosphate and also with iodic acid; (vii) an anode vessel closed at the bottom with membranes was fitted to the top of the cathode U-tube; Pt electrodes. In the experi-

ments with potassium cyanide, sodium platinichloride, and potassium gold chloride, the silver anode was placed at the top and surrounded with the solution of potassium cyanide.

In the second column are given the number of grams of water in which one gram of salt was dissolved. In the sixth column are recorded the weights of the anode portions (including protecting solutions if any).

$K_2C_2O_4$	4.18		1.1g Ag	vi	26g	1ex	a	.441
$KCrO_4$	9.54		1.4g Ag	vi	23g	1ex	a	.512
$K_2Cr_2O_7$	14.6		0.4g Ag	iv	8g	1ex	a	.502
$KClO_4$	119		0.3g Ag	iv	220g	1ex	a	.463
$KClO_3$	26.6		0.4g Ag	iv	60g	1ex	a	.445
	115		0.4	iv	220g	1	a	.462
KCN	7.66		0.4g Ag	iv	12g	1ex	a	.457
	105		0.15	iv	51g	1	a	.47–
NaCl	3.47	13°	1.0g Ag	iv	11g	1ex	a	.648
	5.54	9°	0.9	iv	11g	2	a	.647
	20.7	16°	1.1	iv	33g	1	a	.634
	105	17°	0.4	iv	33g	1	a	.628
	315	6°	0.5	iv	210g	4	a	.620
NaI	22.1		0.4g Ag	iv	31g	1ex	a	.626
Na_2SO_4	11.8	9°	0.9g Ag	iv	34g	1ex	a	.641
	50.7	9°	0.6	iv	32g	1	a	.634
$NaNO_3$	2.07		1.2g Ag	iv	15g	1ex	a	.588
	2.99	9°	0.8	iv	11g	1	a	.600
	34–128	12°	0.4	iv	55–210g	4	a	.614
$NaC_2H_3O_2$	2.81	8°	1.0g Ag	iv	10g	1ex	a	.415
	7.18	13°	0.5	iv	10g	1	a	.421
	41.3	6°	1.2	iv	210g	1	a	.424
	84.6	11°	0.6	iv	210g	1	a	.443
$BaCl_2$	3.2–3.8	6–14[c]	1g Ag	iv	12g	4ex	a	.662
	8.39	19°	1.7	iv	35g	1	a	.642
	79.6	20°	0.4	iv	60g	1	a	.616
	126	10°	0.4	iv	211g	2	a	.614
$Ba(NO_3)_2$	16.2	8°	0.2g Ag	iv	59g	1ex	a	.641
	56.5	14°	0.14	iv	59g	1	a	.620
	134	11°	0.6	iv	211g	1	a	.602
$CaCl_2$	1.70	20°	0.7g Ag	iv	12g	1ex	a	.780
	2.07	12°	0.S	iv	12g	1	a	.771
	2.36	3°	0.7	iv	12g	1	a	.765
	2.74	10°	1.4	iv	12g	1	a	.749
	3.95	21°	1.0	iv	12g	1	a	.727
	21–229	20°	0.3	iv	32–58	2	a	.683
	138	9°	1.2	iv	215g	1	a	.673

CaI_2	1.32		0.8g Ag	iv	16g	1ex	a	.732	
$Ca(NO_3)_2$	1.42	7°	0.7g Ag	iv	12g	1ex	a	.718	
	3.96	7°	1.7	iv	12g	1	a	.652	
	112	7°	0.9	iv	215g	1	a	.613	
$MgCl_2$	2.48	6°	0.4g Ag	iv	11g	1ex	a	.806	
	3.7	15°	1.2	iv	11–37	2	a	.778	
	22.2	14°	0.8	iv	32g	1	a	.706	
	128–241	6–15°	0.4	iv	58–213	2	a	.677	
$Mg\ I_2$	0.796		1.1g Ag	iv	16g	1ex	a	.777	
$MgSO_4$	5.28	4°	1.4g Ag	iv	10g	1ex	a	.762	
	209	5°	0.5	iv	212g	1	a	.656	
$MnCl_2$	3.31	7°	1.4g Ag	iv	11g	1ex	a	.758	
	190	9°	0.5	iv	213g	1	a	.682	
$ZnSO_4$	2.52		0.7g Ag	iv	16g	1ex	a	.778	
	4.05		1.0	iv	14g	1	a	.760	
	267		0.3	iv	220g	1	a	.636	
$FeCl_3$	2.07		1.3g Ag	vii	14g	1ex	c	.746	
	25.2		0.2	vii	20g	1	c	.600	
$AlCl_3$	22.7		0.4g Ag	iv	12g	1ex	a	.714	
UO_2Cl_2	10.4		0.4g Ag	iv	26g	1ex	a	.868	
Morphine H.Cl	54.9		0.3g Ag	iv	92g	1ex	a	.815	
Strychnine H.Cl	55.7		0.5g Ag	iv	93g	1ex	a	.861	
HCl	2.91		1.3g Ag	iv	13g	1ex	a	.319	
	9.86	7°	1.3	iv	9g	1	a	.193	
	36.2	8°	0.4	iv	9g	1	a	.168	
	82.3	8°	0.5	iv	56g	1	a	.161	
	141		1.4	iv	220g	1	a	.171	
	321	8°	0.3	iv	212g	1	a	.216	
	2126	6°	0.3	iv	214g	1	a	.210	
$SnCl_4$[1]	13.5		0.4g Ag	vii	12g	1ex	c	.180	
HBr	8.65		0.7g Ag	iv	10g	1ex	a	.178	
HI	4.82		0.7g Ag	iv	13g	1ex	a	.201	
	117		0.4	iv	88g	1	a	.258	
H_2SO_4	0.557		1.7g Ag	v	19g	1ex	a	.40c	Pt anode
	1.438		2.6	v	15g	1	a	.288	" "
	5.42		1.3	iv	10g	1	a	.174	Cd "
	23.3		0.9	iv	58g	1	a	.177	" "
	98		0.6	iv	172g	1	a	.212	" "
	161		0.4	iv	174g	1	a	.206	" "
HIO^3	13.3		0.2g Ag	vi	25g	1ex	a	.102	Ag "
$Na_4P_2O_7$	35.6		0.4g Ag	vi	22g	1ex	a	.645	" "
Na_2PO_4	26–19		0.4–0.6	vi	23g	2ex	a	—[2]	" "
$Na.PO_3$	10.6		0.5g Ag	iv	13g	1ex	a	.573	

[1] Regarded by Hittorf as 1 part HCl in 24.3 parts water.

[2] Current carried mostly by alkali resulting from hydrolysis.

$K_4.Fe(CN)_6$	5.30		0.6g Ag	vii	23g	1ex	a	.482	
$K.Ag(CN)_2$	7.71		0.5g Ag	vii	21g	1ex	c	.406	
$Na_2.PtCl_6$	1.87		0.6g Ag	vii	14g	1ex	c	.562	
	13.1		0.4	vii	22g	1	c	.519	
$KCl.AuCl_3$	6.08		0.3g Ag	vii	12g	1ex	c	—	
	35.9		0.2	vii	21g	1	c	—	
$KCl.HgCl_2$	7.37		0.5g Ag	vii	24g	1ex	c	—	
$KCl.2HgCl_2$	8.19		0.3g Ag	vii	23g	1ex	c	—	
$KCl.4HgCl_2$	9.59		0.2g Ag	vii	23g	1ex	c	—	
$K.CdI_3$	0.327		1.0g Ag	vii	25g	1ex	c	.43–	
$KCd.I_3$	2.30		0.6	ii	12g	1ex	a	.79–[1]	
	58.7		0.3	ii	87g	1	a	.560	
$K.(C_2H_5)SO_4$	6.55		0.3g Ag	iv	9g	1ex	a	.302	
$Na_2.HPO_4$	20–31		0.6g Ag	vi	22g	1ex	a	.516	
$K.H_2PO_4$	7.59		1.0g Ag	vi	25g	1ex	a	.277	
	10.3		0.7	vi	25g	1	a	.266	
$Na.H_2PO_4$	5.71		0.9g Ag	vi	26g	1ex	a	.383	
CdI_2	1.83		0.3g Ag	ii	18g	1ex	a	1.258	
	3.04	11°	0.7	ii	16g	1	a	1.192	
	4.28	12°	0.7	ii	16g	1	a	1.14–	
	18.1	11°	0.4	ii	14g	1	a	.931	
	69.6		0.2	ii	222g	1	a	.642	
	167	10°	0.3	ii	220g	1	a	.613	
ZnI_2	0.664		2.0g Ag	ii	23g	1ex	a	1.157	Zn anode
	2.457		2.1	ii	16g	1	a	.727	" "
	112.9		0.4	ii	220g	1	a	.675	" "
$ZnCl_2$	2.77		1.8g Ag	ii	16g	1ex	a	1.08—	" "
	333		0.4	ii	219g	1	a	.700	" "
$CdCl_2$	1.27	7–11°	0.8g Ag	ii	17g	3ex	a	1.015	
	1.98	7°	1.7	ii	14g	1	a	.873	
	2.76	10°	1.1	ii	17g	1	a	.779	
	3.36	10°	0.5	ii	13g	1	a	.772	
	5.76		1.0	ii	12g	1	a	.744	
	98.7	8°	0.6	ii	220g	1	a	.725	
	192	11°	0.5	ii	222g	1	a	.708	
CdI_2	1.107		0.2g Ag	ii	16g	1ex	a	2.102	Ethyl alcohol
	1.394		0.3	ii	15g	1	a	2.001	" "
	1.695		0.4	ii	14g	1	a	1.909	" "
	2.190		0.4	ii	25g	1	a	1.848	" "
	2.466		0.3	ii	32g	1	a	1.827	" "
	2.466		0.3	ii	33g	1	a	1.819	" "
	8.375		0.3	ii	11g	1	a	1.552	" "
	37.23		0.1	ii	29g	1	a	1.318	" "

[1] For interpretation and recalculation of these results see J. W. McBain—Zeit. f. Elektrochem., *11*, 215. 1905.

ZnI_2	0.520	0.7g Ag	ii?	21g	1ex	a2.161	Zn	an.	Ethyl alc.
	0.707	0.9	ii?	19g	1	a2.008	"		"
	1.533	0.8	ii?	15g	1	a1.711	"		"
	1.534	0.6	ii?	15g	1	a1.705	"		"
	4.933	0.2	ii?	11g	1	a1.254	"		"
	16.14	0.2	ii?	30g	1	a .747	"		"
$ZnCl_2$	1.74	0.9g Ag	ii?	13g	1ex	a1.998	"		"
	6.79	0.5	ii?	10g	1	a1.538	"		"
CdI_2	3.179	0.1g Ag	ii?	11g	1ex	a2.3—	Amyl alcohol		

1868. E. Bourgoin.

Du role de l'eau dans l'electrolyse. Ann. Chim. Phys. (4), *15*, 47.

Apparatus: capacity 40 c.c.

I have deduced the following migration values from the experimental data afforded by the work of the author; the calculation is based (incorrectly) upon the change in constant volume of solution, not upon a constant weight of solvent.

KOH	1.68m	1ex	ac.746
	1.14	1ex	ac.749
H_2SO_4	0.2–0.5m	3ex	ac.168
HNO_3	1.66m	1ex	a .126

1868. E. Bourgoin.

De l'electrolyse des acides organiques et de leurs sels. Ann. Chim. Phys. (4), *14*, 157.

In this extended investigation carried out from another standpoint, in no case are sufficient data afforded to permit of the deduction of migration values, unless possibly in the case of succinic acid (n .6– – or .3– – ?).

1870. E. Bourgoin.

Mémoire sur l'inegalité des pertes d'acide et de sel dans le voisinage des pôles. Ann. phys. Chim. (4), *21*, 264.

The author rejects Hittorf's explanation of the changes of concentration during electrolysis in favor of that of d'Almeida; and classifies the acids according as the acidity at the anode increases or decreases by electrolysis.

The details of two experiments with oxalic acid are given. In the first, the loss of acid at the cathode was one third of that corresponding to the hydrogen collected from that electrode. In the second, the loss of acid was three times as great at the cathode as at the anode.

1878. M. Kirmis.

Zur Wanderung der Ionen. Wied. Ann., *4*, 503.

For apparatus see Wiedemann, 1856; capacity 110 c.c.; no diaphragms. The siphon became considerably heated. No middle portion; anode Cu, and cathode Pt.

The calculation is incorrect (based on constant volume of solution, not constant amount of water).

$CuSO_4$	5.06	percent	15°	4.5g Ag	3ex	c.723	
	4.83	"	4°	2.7	3ex	c.713	
	3.52	"	22°	5.9	3ex	c.702	
	3.17	"	13°	4.8	3ex	c.690	
	2.20	"	24°	2.0	3ex	c.686	
	1.75	"	23°	2.1	3ex	c.685	
	1.04	"	22°	3.5	3ex	c.655	
	0.497	"	9°	1.5	3ex	c.641	
	1–5	"	0–8°	—	4ex	c.780	Pt anode

1881. J. Kuschel.

Die Bestimmung der Ueberführungszahlen der Ionen für Lithium- und Kohlensäureverbindungen. Wied. Ann., *13*, 289; Dissert. Breslau.

Apparatus: (i) superposed glasses; diaphragms of gold-beaters' skin. The Pt cathode was surrounded by free acid, the anode was of Cd; the middle portion was tested for free acid and for Cd. (ii) a U-shaped cathode tube with three superposed glasses; capacity 25–60 c.c.; Pt electrodes. In the experiments with the carbonates the middle portion was tested for neutrality by litmus after precipitation by barium chloride. For the experiments with the caustic alkalis, porous earthenware was substituted for the diaphragms of gold-beaters' skin.

The method of calculation is correct.

KCl	13–0.23%		—g Ag	i	4ex	.518
LiCl	6.89m	18°	0.4g Ag	i	1ex	a.773
	3.21	21°	0.5	i	2	a.753 ± 2
	1.78	19°	0.4	i	2	a.738 ± 9
	0.809	17°	0.4	i	4	a.739 ± 7
	0.235	15°	0.2	i	2	a.718 ± 8
	0.118	14°	0.5	i	1	a.694
	0.103	13°	0.4	i	1	a.705
	0.046	16°	0.4	i	1	a.670
	0.039	17°	0.3	i	1	a.679
LiI	3.12m	17°	0.2	i	1ex	a.719
	1.41	20°	0.2	i	2	a.712 ± 4

	0.67	17°	0.2	i	2	a.727 ± 17
	0.66	19°	0.2	i	1	a.700
	0.33	19°	0.2	i	2	a.706 ± 1
	0.074	16°	0.2	i	3	a.692 ± 9
	0.037	14°	0.14	i	3	a.702 ± 9
	0.014	14°	0.1	i	2	a.682 ± 2
K_2CO_3	8.112m	26°	0.5g Ag	ii	2ex	c.341 ± 0
	3.15	23°	0.8	ii	2	c.404 ± 1
	1.61	22°	0.5	ii	2	c.416 ± 0
	0.764	22°	0.3	ii	2	c.437 ± 7
	0.441	24°	0.2	ii	1	c.434
	0.151	21°	0.2	ii	2	c.377 ± 3
	0.074	24°	0.14	ii	2	c.372 ± 4
	0.029	24°	0.07	ii	2	c.302 ± 7
Na_2CO_3	2.84m	23°	0.4g Ag	ii	2ex	c.530 ± 1
	0.985	23°	0.4	ii	2	c.548 ± 0
	0.189	24°	0.2	ii	2	c.519 ± 0
	0.093	24°	0.1	ii	2	c.474 ± 7
Li_2CO_3	0.232m	25°	0.2g Ag	ii	2ex	c.582 ± 5
	0.136	21°	0.2	ii	2	c.593 ± 9
Li_2SO_4	0.159m	23°	0.2g Ag	ii	2ex	c.649 ± 4
	0.090	22°	0.1	ii	2	c.595 ± 3
KOH	0.804m	23°	0.6g Ag	ii	2ex	c.739 ± 8
	0.190	27°	0.3	ii	2	c.730 ± 0
	0.103	22°	0.2	ii	2	c.742 ± 10
NaOH	1.084m	25°	0.6g Ag	ii	2ex	c.827 ± 4
	0.285	23°	0.3	ii	2	c.800 ± 5
	0.108	21°	0.1	ii	2	c.843 ± 4
LiOH	1.495m	25°	0.4g Ag	ii	1ex	c.890
	0.402	21°	0.4	ii	2	c.863 ± 3
	0.201	21°	0.4	ii	2	c.848 ± 9

1882. R. Lenz.

Ueber das galvanische Leitungsvermögen alkoholischer Lösungen. Beiblätter, *7*, 399, from Mém. de St. Pétersb. (7), *30*, 64.

The transference of the iodine in aqueous and alcoholic solutions of CdI_2 and of KI was determined in an apparatus consisting of an H-tube fitting on top of an anode vessel. The contents of the latter were analyzed, The following table contains the values of n for iodine obtained by the author by interpolation from his experiments. The percent of alcohol in the solutions is given at the head of the column, the concentration of the CdI_2 in the first column.

The method of calculation is based (wrongly) on constant volume of solution.

	0	5	10	15	20	25	30
½m	1.135	1.110	1.089	1.073	1.072	1.077	1.088
¼m	1.044	1.021	1.017	1.022	1.032	1.044	1.057
⅛m	0.929	0.914	0.915	0.922	0.934	0.952	0.974
1/16m	0.808	0.818	0.831	0.851	0.876	0.899	0.928
	35	40	45	50	55	60	65
½m	1.108	1.130	1.160	1.193	1.226	1.262	1.300
¼m	1.070	1.088	1.120	1.159	1.192	1.229	1.265
⅛m	1.000	1.028	1.058	1.089	1.121	1.160	1.198
1/16m	0.959	0.989	1.019	1.052	1.088	1.127	1.170
	70	75	80	85	90	95	
½m	1.338	1.378	1.417	1.460	1.502	1.549	
¼m	1.305	1.344	1.384	1.427	1.471	1.515	
⅛m	1.239	1.282	1.329	1.375	1.421	1.470	
1/16m	1.212	1.262	1.306	1.357	1.404	1.458	

With solutions of potassium iodide the values $n = .511$ to $n = .520$ were found independent of the concentration and of the amount of alcohol present.

The experiments with potassium chromate were carried out in a slightly modified apparatus, in which a Pt cathode surrounded by potassium carbonate solution, and a Mg anode were employed; $n = .46 -$ to $n = .51 -$ independent of the concentration and of the percent of alcohol.

The paper further contains a number of measurements of conductivity and diffusion.

1885. **J. Moser.**

Elektrische und thermische Eigenschaften von Salzlösungen. Wien. Sitzungsber., *92*, Abth. II, 652.

The author calculated the migration values by means of the formulæ of Helmholtz from the E.M.F. of concentration cells with and without diffusion.

$ZnCl_2 + 100\ H_2O$ and $ZnCl_2 + 750\ H_2O$ $\quad 1ex\ .71-$
$ZnSO_4 + 100\ H_2O$ and $ZnSO_4 + 800\ H_2O$ $\quad 1ex\ .64-$

1886. **O. Lodge.**

On the Migration of Ions and an Experimental Determination of Absolute Ionic Velocity. Brit. Assoc. Rep., 1886, 389.

In the following series of experiments, two cups were connected by a horizontal siphon. When the current was passed through, the ions from the cups moved through the siphon, their progress being followed by a color change or by the formation of a precipitate.

Cups.		*Siphon.*		
$BaCl_2$, Na_2SO_4	10%	6% HCl, litmus	23ex	$Ba/SO_4 = \frac{1}{1}$
$BaCl_2$, Na_2SO_4	5%	6% HCl, litmus	14ex	$Ba/SO_4 = \frac{1}{1}$
$BaCl_2$, Na_2SO_4	5%	$C_2H_4O_2$, agar agar	9ex	$Ba/SO_4 = \frac{1}{1}$
$BaCl_2$, NaCl		$C_2H_4O_2$, H_2SO_4, $AgNO_3$, agar agar	4ex	$Ba/Cl = \frac{1}{2}$
$BaCl_2$, KI		$C_2H_4O_2$, H_2SO_4, $AgNO_3$, agar agar	5ex	$Ba/I = \frac{1}{2}$
$BaCl_2$, KBr	10%	$C_2H_4O_2$, H_2SO_4, $AgNO_3$, agar agar	3ex	$Ba/Br = \frac{1}{2}$
$SrCl_2$, NaCl	10%	$C_2H_4O_2$, H_2SO_4, $AgNO_3$, agar agar	2ex	$Sr/Cl = \frac{1}{2}$
$SrCl_2$, KBr	10%	$C_2H_4O_2$, H_2SO_4, $AgNO_3$, agar agar	2ex	$Sr/Br = \frac{1}{2}$
$SrCl_2$, KI	10%	$C_2H_4O_2$, H_2SO_4, $AgNO_3$, agar agar	2ex	$Sr/I = \frac{1}{2}$
$CuSO_4$, H_2SO_4		NaCl, $BaCl_2$, NaOH, phenol phthalein	3ex	$H^1/SO_4 = \frac{1}{1}$
$CuSO_4$, $CuSO_4$		NaCl, K_4FeCy_6	1ex	
$CuSO_4$, NaOH		NaCl, phenol phthalein	1ex	[2]
$(NH_4)_2SO_4$, —		NaCl, Nessler solution	1ex	

1888. M. Loeb and W. Nernst.

Zur Kinetik der in Lösung befindlichen Körper. Zeit. phys. Chem., *2*, 948.

Apparatus similar to Gay-Lussac's burette, with side tube at top for cathode; anode at bottom; capacity 60 c.c.; Ag electrodes. In preliminary experiments with silver nitrate the loss in the whole apparatus was 0.06 percent, the loss in the middle portions was 0.5–0.7 percent; no diaphragms; method of calculation correct.

The paper further contains a number of conductivity measurements in confirmation of Kohlrausch's law.

$AgNO_3$	0.1043m	20°	0.08g Ag	1ex	ac.528
	0.0521	26°	0.08	1	ac.524
	0.025	26°	0.05	1	ac.522
	0.025	0°	0.05	1	ac.538
	0.0105	26°	0.03	2	ac.522 ± 2
$AgClO_3$	0 0245m	25°	0.05g Ag	2ex	ac.501 ± 2
$AgClO_4$	0.0247m	25°	0.04g Ag	2ex	ac.513 ± 2
$Ag(C_2H_5)SO_4$	0.0243m	25°	0.05g Ag	2ex	ac.387 ± 2
	0.0061	25°	0.02	1	ac.384
$C_{10}H_7.SO_3.Ag$	0.0129m	29°	0.03g Ag	1ex	ac.390
	0.0250	25°	0.04	1	ac.386
$C_6H_5.SO_3.Ag$	0.0250m	25°	0.04g Ag	2ex	ac.347 ± 4
$C_2H_3O_2Ag$	0.0097m	25°	0.02g Ag	2ex	ac.376 ± 1
Ag_2SiFl_6	0.0282m	22°	0.05g Ag	2ex	ac.465 ± 2
$Ag_2S_2O_6$	0.0246m	25°	0.04g Ag	3ex	ac.605 ± 1
	0.0246	0°	0.05	2	ac.604 ± 1

[1] Absolute velocity of H ion = 0.0027.

[2] "OH nearly as quick as H."

$C_8H_{11}.SO_3.Ag$	0.0238m	24°	0.06g Ag	1ex	ac.293
	0.0222	29°	0 04	1	ac.295
	0.0222	0°	0.04	2	ac.273 ± 0

1889. C. L. Weber.

Ueber absolute Geschwindigkeit der Ionen. Zeit. phys. Chem., *4*, 182.

The author deduced the following migration values from measurements of the limiting current density at which normal products appear at the electrodes and above which secondary reactions occur. The third column below gives the velocities in mm. per second.

$CuSO_4$	$\frac{1}{2}$ of 80.16g Cu per litre	0.017
	$\frac{1}{4}$ of 80.16g Cu per litre	0.023
	$\frac{1}{8}$ of 80.16g Cu per litre	0.024
	$\frac{1}{16}$ of 80.16g Cu per litre	0.028
	$\frac{1}{32}$ of 80.16g Cu per litre	0.021
	$\frac{1}{64}$ of 80.16g Cu per litre	0.022
	$\frac{1}{128}$ of 80.16g Cu per litre	0.033
	$\frac{1}{256}$ of 80.16g Cu per litre	0.042
$CdSO_4$	0.1 m	0.023
	0.04	0.029
	0.02	0.026
	0.01	0.036
	0.005	0.045
	0.0025	0.051
$Zn(NO_3)_2$	0.2 m	0.091
	0.1	0.111
	0.04	0.095
	0.02	0.077
	0.01	0.084
	0.005	0.051
	0.0025	0.052
	0.0012	0.051

1890. A. Chassy.

Nouveau Transport Électrique. Ann. chim. phys. (6), *21*, 241.

The author determined the movement of one component of mixtures of salts in aqueous solution. Misled by assuming that the decomposition products at the electrodes indicated the salt that had carried the current, he had to explain the observed movement of the other salts present by the assumption of the movement of non-dissociated molecules. In the following list the first salt was in each case the only one measured. Many cases are omitted in which only one component of the mixture was indicated. For summary see Ponsot — Comptes rendus, *138*, 192.

Sulphates of Zn, Cu.
" " Zn, Cd.
" " Zn, Ag.
" " Zn, Na, Mg, Cu.
" " Zn, Cu, Ni, K.
Nitrates " Ba, Ag.
" " Ba, Cu.
" " Ba, Ni.
" " Ba, Zn.
" " Ba, K, Cu.
" " Ba, K, Cu, Na, Zn, Mg, Co, Ag.
" " Pb, Ba, Zn, K.
" " Cu, Ba, Ag, K.
Chlorides " K, Zn.
" " Ca, Na, Zn, Cu.
" " Zn, Ba, Mg, K.
Sulphates " K, Cd, Cu, with acetate of Zn.
K_2SO_4, $Zn(C_2H_3O_2)_2$.
$Zn(C_2H_3O_2)_2$, K_2SO_4, Na_2SO_4, $NaC_2H_3O_2$.

1890. **W. Kistiakowsky.**

Die wässerigen Lösungen von Doppelsalzen. Zeit. phys. Chem., *6*, 97.

Apparatus a knee-shaped burette; capacity 100 c.c.; Ag electrodes; no diaphragms; middle portion unchanged. The concentrations are expressed in mols per 1000g solution.

$AgNO_3$	0.0189	15°	0.04g Ag	1ex	ac.531
$Ag_3Cr(C_2O_4)_3$	0.022	14°	0.05g Ag	3ex	ac.57- ± 18

1892. **W. Bein.**

Beiträge zur experimentellen Bestimmung von Ueberführungszahlen in Salzlösungen. Wied. Ann., *46*, 29.

Apparatus of three types, capacity 55–90g, *viz.*; (i) superposed glasses with diaphragms of fish bladder (B), or usually of porous earthenware (E); (ii) a winding spiral and U-tube, no diaphragms; (iii) a knee-shaped burette.

In experiments with $CuSO_4$, $CdCl_2$, $CaCl_2$, and CdI_2 the voltage was varied from 20–100 volts without affecting the results. In the fifth column below are given the concentration changes in the middle portions; the values in the last column given in ( ) are those obtained by Bein in 1899 by a recalculation.

The method of calculation is correct; the accuracy of the better experiments is estimated to be one or two units in the second decimal place.

$CuSO_4$	0.73% Cu	20–30°	0.06g Cu	0.6–0.06%	i	E	6ex	a.647 ± 24
	0.73	16–19°	0.05	0.5–0.1	ii		2	ac.638 ± 2
	0.76	16–24°	0.06	0.4–0.03	i	B	8	a.79– ± 17
	0.76	74°	0.05	1.5	ii		1	ac.622
KCl	0.41% Cl	18–19°	0.06g Cl	0.1%	i	B	2ex	a.496 ± 3 (.530)
	0.6	74–75°	0.03	0.3	ii		2	ac.509 ± 9
$AgNO_3$	1.85% Ag	13–15°	0.06g Ag	0.5–0.05%	iii		3ex	ac.525 ± 3
	0.6	75–96°	0.06	2–0.4	iii		6	ac.512 ± 6
NaCl	0.92% Cl	7–8°	0.06g Cl	0.3%	ii		2ex	ac.608 ± 3
	0.92	95°	0.05	0.8–0.1	ii		3	ac.551 ± 2
$BaCl_2$	0.84% Cl	12°	0.07g Cl	1–0.3%	ii		2ex	ac.580 ± 2
	0.84	89°	0.07	0.5	ii		1	ac.565
	0.58	74°	0.05	0.6	ii		1	ac.580
CdI_2	0.68% I	20°	0.1g I	1–0.4%	i, ii	E	3ex	ac.65– ± 25 (.652)
	0.68	76°	0.06	1.5	ii		2ex	ac.600 ± 13
$CdCl_2$	0.9% Cl	8°	0.05g Cl	0.7%	ii		2ex	ac.567 ± 2
	0.6	21°	0.6	0.6–0.01	i	E	4	a.546 ± 20 (.557)
	0.87	96–97°	0.07	0.8–0.5	ii		2	ac.570 ± 5
$CaCl_2$	0.8% Cl	9°	0.05g Cl	1–0.1%	ii		2ex	ac.602 ± 2
	0.45	16°	0.08	0.3–0.04	i	B	6	a.610 ± 16 (.638)
	0.85	94°	0.04	0.2	ii		1	ac.549

1892. W. C. D. Whetham.

Ionic Velocities. Proc. Roy. Soc., *52*, 284. Zeit. phys. Chem., *11*, 220. Phil. Trans., *184*, A, 337.

The author measured the velocity of the meniscus between pairs of solutions of electrolytes, first with direct, and then with reversed current. The apparatus consisted of two vertical tubes joined by a third much narrower tube bent parallel to the others for the greater part of its length. Two solutions of equal specific resistance were placed in the apparatus, the specifically heavier below the other. The surface of contact lay in the narrow vertical tube, where the fall of potential per cm. could be determined.

In the following table, the salts experimented with are named in the first column, and in the succeeding columns in order are given the concentrations, the solvent (W = water, Am = aqueous ammonia, Al = "alcohol of 0.05 strength"), the ion to which the rate of the meniscus movement was ascribed, the number of experiments, the observed velocity in cm. per second per unit

potential fall, and the velocity calculated from Kohlrausch's conductivity measurements and Hittorf's migration determinations. In the case of the alcoholic solutions, for lack of migration determinations, the sum of the observed ionic velocities is compared with that calculated from the conductivity.

$CuCl_2$ and NH_4Cl	0.18m	Am	Cu	1ex	0.00026	0.00031
$CuCl_2$ and NH_4Cl	0.1	Am	Cl	1ex	0.000309	0.00031
KCl and $KMnO_4$	0.0046m	W	Cl	1ex	0.00057	0.00053
KCl and $KMnO_4$	0.046	W	Cl	1ex	0.00059	0.00053
$K_2Cr_2O_7$ and K_2CO_3	0.1m	W	Cr_2O_7	3ex	0.00047	0.00047
$K_2Cr_2O_7$ and KCl	0.1	W	Cr_2O_7	1ex	0.00044	0.00047
$Co(NO_3)_2$ and $CoCl_2$	0.05m	Al	Cl	2ex	0.000026	0.000060
$CoCl_2$ and $CaCl_2$	0.05m	Al	Co	2ex	0.000022	
			NO_3		0.000035	0.000079
$Co(NO_3)_2$ and $Ca(NO_3)_2$		Al	Co	1ex	0.000044	

1893. S. Lussana.

Einfluss der Temperatur auf die elektromotorische Kraft der Concentrationselemente und die Wanderung der Ionen. Beiblätter, *17*, 218, from Atti del R. Ist. Venet., Ser. VII, *3*, 1111 (1892).

Apparatus: Horizontal tube bent into five parallel portions, with vertical tubes sealed on at the ends and at the middle; 3 (?) middle portions.

The author found the migration of the cation $(1-n)$ proportional to the absolute temperature (T). In the second column below is given the weight of salt in 100g water; in the third the value found for $10^7(1-n)/T$; and in the last the transport of the anion at 0° C.

$ZnSO_4 7H_2O$	57.694–2.319	26632–25244	.27–.31
$CuSO_4 5H_2O$	5.008–0.712	24627–22076	.33–.40
$Pb(NO_3)_2$	26.512–4.618	18955–15982	.48–.53

1893. S. Sheldon and G. M. Downing.

Die kritische Stromdichtigkeit für Kupferniederschläge und die absolute Geschwindigkeit der Wanderung der Ionen. Beiblätter, *17*, 1090, from Phys. Rev., *1*, 51.

The author deduced the migration values from measurements of the limiting current density at which normal products appear at the electrodes, and above which secondary reactions occur. The velocity is presumably in cm. per second for unit potential fall.

$CuSO_4$	0.1–1.89m	0.00020–0.000445

1894. A. Campetti.

Ueber den Einfluss des Lösungsmittels auf die Geschwindigkeit der Ionen. Beiblätter, *18*, 942 (from Nuov. Cim. (3), *35*, 225).

LiCl	water	ac.705
	ethyl alcohol	ac.71–
	methyl alcohol	ac.64–
$AgNO_3$	water	ac.518
	ethyl alcohol	ac.51–
	methyl alcohol	ac.47–

1894. S. Lussana.

Einfluss von Magnetismus und Wärme auf die Wanderung der Ionen. Beiblätter, *18*, 364; (from Atti R. Ist. Veneto (7), *4*, 13 pp., 1893, Sepab.).

An extension of the author's work of the year before, with the same apparatus. In solutions of $NiSO_4$, NaCl, KCl, and $CuCl_2$ the relative velocity of the cation $(1-n)$ is proportional to the absolute temperature.

In order to ascertain whether magnetism exerts any noticeable influence on the transport, measurements were made of the rate of motion of the meniscus between acidified solutions of ferrous and cupric sulphates in and out of the magnetic field. The author finds that magnetism probably slightly reduces the rate of the ferrous ion; the resistance of ferrous sulphate solution is not noticeably affected by a magnetic field whose lines of force are perpendicular to the direction of the current.

1894. W. C. D. Whetham.

On the Velocities of the Ions and the Relative Ionization-power of Solvents. Phil. Mag., *38*, 392.

For apparatus, method and explanation of the following table, see Whetham, 1892. In these experiments the solutions were solidified with agar agar jelly. In the experiment with sodium acetate one half of the solution was colored red by caustic soda, the other half "decolorized by means of a few drops of dilute acetic acid." A measurement was made of the rate of motion of the red color at the boundary between solutions of ferric chloride and ferric acetate (containing ferric chloride); in order to explain his results the author ascribed the color to colloidal ferric hydrate, and adduced a number of conductivity measurements and experiments with dialyzed iron, in support of this view.

$K_2Cr_2O_7$ and K_2CO_3	0.1 m	W	Cr_2O_7	1ex	0.00044	0.00047
$NaC_2H_3O_2$	0.07m	W	H	1ex	0.000065	0.00030

1895. W. C. D. Whetham.

On the Velocities of the Ions. Phil. Trans., *186*, *A*, 507.

An extension of the author's work in 1892 and 1894. The same apparatus was employed. The solutions were solidified by the use of agar agar. The rate of extension of the precipitate formed at the surface of contact was measured; the current being passed in one direction only. The experiments were carried out at from 8–17° and corrected for 18°. The solutions were 0.1 m.

$BaCl_2$; and NaCl + " a little " Na_2SO_4	Ba	2ex	0.000389	0.000366
$CaCl_2$; and NaCl + " considerable " Na_2CO_3	Ca	1ex	0.000349	0.000290
$AgNO_3$; and $NaNO_3$ + " a little " NaCl	Ag	1ex	0.000488	0.000462
Na_2SO_4; and NaCl + $BaCl_2$	SO_4	2ex	0.000447	0.000492

1896. C. Cattaneo.

Ueber den Einfluss des Lösungsmittels auf die Geschwindigkeit der Ionen. Beiblätter, *21*, 749 (from Rendic. R. Acc. dei Lincei (5), *5*, 2 Sem. 207; *6*, 1 Sem. 279. Nuovo Cim. (4), *6*, 140.)

With sodium chloride and ammonium chloride a Pt cathode and a Zn or Cd anode was used; with hydrochloric acid the anode was of Au or Cu.

NaCl	water	.66–
	glycerine	.64–
NH_4Cl	water	.51–
	glycerine	.57–
HCl	water	.224
	ethyl alcohol	.205
	methyl alcohol	.236
	amyl alcohol	.240
	glycerine	.237
	ethyl alcohol with chloroform	.209
	ethyl alcohol with chloroform and ethyl ether	.218

1896. Th. DesCoudres.

Messungen der elektromotorischen Kraft Colley' schen Gravitationselemente. Wied. Ann., *57*, 232.

From measurements of the E.M.F. of gravitation cells with electrodes of Hg/Hg_2Cl_2 the author deduced the following values for n.

NaCl	19.9 percent	.66–
$BaCl_2$	17.0 "	.64–
LiCl	17.3 "	.77–
KCl	16.8 "	.50–
HCl	3.56 "	.150
$CdCl_2$	30.1 "	1.02–1.10

1896. A. Rosenheim.

(Experiments by W. Bein.) Ueber die Einwirkung anorganischer Metallsäuren auf organische Säuren. Zeit. anorg. Chem., *11*, 175, 225.

Apparatus: two U-tubes connected by a siphon; capacity 108g; Pt electrodes; no diaphragms; no middle portion. The object of the investigation was to determine the constitution of these complex compounds. Concentration 1–2 percent; one experiment each; 18° C. In the last column is given the component analyzed. C_2O_3, Mo, W, and V moved in all cases toward the anode.

$(NH_4)_2O.2MO_3$	0.3g Ag	ac { .530 MO_3 / .539 NH_3
$MO_3.C_2O_3.3H_2O$	0.08g Ag	ac { .47– C_2O_3 / .48– MO_3
$K_2O.WO_3.C_2O_3.H_2O$	0.2g Ag	ac { .306 C_2O_3 / .327 WO_3 / .540 K
$(NH_4)_2O.2C_2O_3.2MO_3.3H_2O$	0.3g Ag	ac { .40– C_2O_3 / .40– MO_3
$(NH_4)_2O.2MO_3.C_2O_3$	0.2g Ag	ac .33– C_2O_3
$3(NH_4)_2O.V_2O_5.4C_2O_3.4H_2O$	0.02g Ag	ac { .36– C_2O_3 / .36– V_2O_5
"	0.1g Ag	ac .39– C_2O_3
$3K_2O.Al_2O_3.6C_2O_3.5H_2O$	0.4g Ag	ac .50– C_2O_3
$3K_2O.Cr_2O_3.6C_2O_3.6H_2O$	0.6g Ag	ac .33– C_2O_3
$K_2O.Al_2O_3.4C_2O_3.7\frac{1}{2}H_2O$	0.3g Ag	ac .39– C_2O_3

1897. V. Gordon.

Ueber die Abhängigkeit der Ueberführungszahlen des Kadmium in wässerigen Lösungen von der Temperatur. Zeit phys. Chem., *23*, 469.

Apparatus: N-tube fitting into the top of an Erlenmeyer flask; capacity 100 c.c.; anode Cd, cathode Hg; no diaphragms; method of calculation correct.

$CuSO_4$	9–10 percent		0.6g Ag	0.07 percent	2ex	a	$.720 \pm 6$
$CdSO_4$	11.4 "	9°	1–2g Ag	0.1 "	3ex	a	$.672 \pm 10$
	11.4 "	40°	1–2	0.1–0.2 "	2	a	$.717 \pm 5$
	12 "	81°	1.9	0.5 "	2	a	$.719 \pm 4$
	34.5 "	9°	1.9	0.2–0.5 "	2	a	$.803 \pm 0$

	34	percent	40°	3	0.1	percent	2	a .810 ± 6
	34	"	69°	3	0.2–0.6	"	2	a .797 ± 15
$CdBr_2$	29.5	"	7°	1 g Ag	0.2–0.01	"	3ex	a .894 ± 5
	29.4	"	39°	1.5	0.5–0.00	"	3	a1.040 ± 34
	29.4	"	75°	2.3	1–0.4	"	3	a .970 ± 25
CdI_2	35	"	40°	1.7g Ag	0.1–0.2	"	2ex	a1.232 ± 8
	35.5	"	74°	2.0	0.17	"	2	a1.231 ± 17

1897. F. W. Küster.

Ueber Ionenreaktionen und ihre Bedeutung für die Elektrochemie. Zeit. f. Elektrochem., *4*, 105.

When a current is passed through a U-tube whose lower half is filled with cupric sulphate solution, while both arms are filled with sodium sulphate solution into which the electrodes are dipped, then the blue layer moves toward the cathode; when the lower solution is Fehling's solution, and the upper Seignette salt, the blue color moves toward the anode, as the copper is contained for the most part in complex anions.

1897. W. J. Mather.

A New Apparatus for Determining the Relative Velocities of Ions; with some Results for Silver Ions. Johns Hopkins Univ. Cir., *16*, No. 130, 45 (1897), Am. Chem. Jour., *26* (1901), 473.

Apparatus: an M-shaped tube provided in the middle with a glass tap of large bore; capacity 90 c.c; Ag electrodes; no diaphragms; no middle portion; calculation based (incorrectly) on constant volume of solution.

$AgNO_3$	0.1 m	0°	0.1 g Ag	3ex	ac.541 ± 0	
	0.1	29°	0.05	1	ac.532	
	0.1	48°	0.15	3	ac.528 ± 1	
	0.025	0°	0.07	1	ac.538	
	0.025	45°	0.08	1	ac.525	
	0.1	24°	0.15	2	ac.532 ± 1	49 percent alcohol.
	0.108	20°	0.05	3	ac.594 ± 2	absolute alcohol.
$AgC_2H_3O_2$	0.025m	0°	0.05g Ag	2ex	ac.373 ± 1	
	0.025	28°	0.03	1	ac.382	
	0.025	46°	0.08	3	ac.389 ± 1	

1897. W. Nernst.

Zwei einfache elektrochemische Vorlesungsversuche. Zeit. f. Elektrochem. *3*, 308.

A 0.003m solution of potassium nitrate is placed in the arms of a U-tube over a solution of potassium permanganate of the

same specific conductivity, weighted with urea. During the passage of the current the red layer moves toward the anode with a velocity within a few percent of that calculated from the conductivity of potassium permanganate.

1897. A. Schrader.

Zur Elektrolyse von Gemischen. Zeit. f. Elektrochem., *3*, 498. Auszug aus Berliner Inaug. Dissert.

Apparatus: an ∽-tube; capacity 150 c.c; no diaphragms.

The paper is mainly devoted to the determination of the transport in aqueous solutions containing a pair of electrolytes, viz.: KCl and KI; H_2SO_4 and $CuSO_4$. In addition the following results of measurements with acetic acid between Ag electrodes are given without experimental details. "The rate of transport of acetic acid seems to become constant only at dilutions where the error of analysis is nearly as great as the quantity measured."

0.79m .362;	0.74m .307;	0.59m .241;
0.48m .212;	0.36m .182;	0.25m .169.

1898. W. Bein.

Zur Bestimmung der Ueberführung bei der Elektrolyse verdünnter wässeriger Salzlösungen. Zeit. phys. Chem., *27*, 1.

Apparatus of various forms, complete, and somewhat complicated; no diaphragms; Pt cathode, Cd anode; method of calculation correct.

The capacities of the apparatus are given in hektograms in the sixth column below, the percent changes in the middle portion in the fifth column.

	Percent.			Percent.			
HCl	0.02–0.05 Cl	9°	0.02g Cl	0.1	1–5	2ex	ac.167 ± 1
	0.035	50°	0.03		5	2	ac.199 ± 0
	0.035	96°	0.03		5	3	ac.252 ± 10
	0.2–0.5	16°	0.03	0.2–2	1	8	ac.170 ± 3
	0.2–0.5	77°	0.04	0	1	3	ac.219 ± 12
	13.9	97°	0.1		½	1	ac.393
NaCl	0.02–0.05 Cl	10°	0.02g Cl	0.0–0.3	7	5ex	ac.615 ± 12
	0.040	51°	0.03		5	2	ac.583 ± 5
	0.040	97°	0.03		1–5	2	ac.547 ± 4
	0.25	76°	0.03		1	1	ac.586
	0.2–0.9	12°	0.03	0.3–5	1	11	ac.613 ± 20
	0.50	76°	0.03	0	1	2	ac.570 ± 5

	0.2–0.9	95°	0.05		1	4	ac.557 ± 4
	12.1	21°	0.3		½	1	ac.677
	14.2	97°	0.14		½	1	ac.567
KCl	0.04–0.5 Cl	11°	0.02g Cl	0.04–4	1–7	5ex	ac.503 ± 20
	0.30	76°		0.6	1	3	ac.510 ± 2
NH_4Cl	0.2 Cl	20°	0.02g Cl	0.6	1	2ex	ac.507 ± 6
RbCl	0.19 Cl	22°	0.02g Cl		1	1ex	ac.515
CsCl	0.18 Cl	20°	0.02g Cl		1	1ex	ac.508
TlCl	0.04 Cl	21°	0.02g Cl		5	1ex	ac.516
LiCl	0.036 Cl	20°	0.03g Cl		5	2ex	ac.624 ± 4
	0.035	97°	0.02		5	2	ac.617 ± 6
	0.2–0.5	20°	0.03		1	6	ac.672 ± 9
	0.20	96°	0.03		1	2	ac.610 ± 9
$CaCl_2$	0.039 Cl	22°	0.03g Cl		1	1ex	ac.553
	0.039	49°	0.03		5	1	ac.555
	0.0391	97°	0.03		5	1	ac.530
	0.204	97°	0.03		1	1	ac.554
	0.425	97°	0.04		1	1	ac.574
	0.20	25°	0.03		1	3	ac.567 ± 40
	0.42	24°	0.04		1	1	ac.595
	0.99	21°	0.05		1	1	ac.610
	14.1	25°	0.26		½	1	ac.718
	14.1	97°	0.13		½	1	ac.79–
$BaCl_2$	0.040 Cl	10°	0.03g Cl		7	2ex	ac.559 ± 1
	0.041	50°	0.03		5	1	ac.525
	0.041	97°	0.03		5	1	ac.515
	0.30	10°	0.04		1	2	ac.570 ± 2
	0.6–1.0	12°	0.06		1	3	ac.585 ± 11
	0.77	96°	0.03		1	1	ac.543
	0.301	76°	0.03		1	2	ac.553 ± 3
	0.202	78°	0.02		1	1	ac.518
$CdCl_2$	0.036 Cl	20°	0.02		5	1ex	ac.557
	0.20	24°	0.02		1	2	ac.568 ± 3
	0.20	96°	0.03		1	2	ac.475 ± 2
	0.50	17°	0.03		1	2	ac.567 ± 11
	13.8	97°	0.12		½	2	ac.963 ± 3
	13.8	24°	0.19		½	1	ac.657
$AgC_2H_3O_2$	0.43 Ag	24°	0.08g Ag		1	1ex	ac.413Pt elec.
	0.43	24°	0.07		1	1	a.385[1] c.414Ag/Pt
	0.43	49°	0.07		1	1	c.412Ag/Pt
	0.43	96°			1	2	c.438 ± 4
$AgNO_3$	0.54 Ag	76°	0.04g Ag	0.2	1	1ex	ac.517
	0.40	96°	0.07		1	1	ac.482
H_2SO_4	0.24 H_2SO_4	11°	0.05g SO_4		1	3ex	ac.175 ± 3
	0.24	23°	0.05		1	1	c.200
	0.24	96°	0.05		1	2	ac.304 ± 1

[1] Superoxide formed at anode.

$CuSO_4$	0.032Cu	1°	0.03g Cu		6	1ex	ac.615
	0.032	15°	0.02		6	1	ac.633
	0.30	0°	0.03		1	1	ac.611
	0.30	50°	0.04		1	1	ac.607
	0.73	15°	0.05		1	1	ac.632
	0.76	74°	0.05		1	1	ac.622
	0.30	97°			1	5	ac.21– to .47–
$SrCl_2$	0.04 Cl	21°	0.03g Cl		5	1ex	ac.560
	0.20	20°	0.03g		1	1	ac.575
$MgCl_2$	0.17 Cl	21°	0.02g Cl		1	1ex	ac.615
$MnCl_2$	0.20 Cl	18°	0.03g Cl	1.5	1	1ex	ac.613
$CuCl_2$	0.18 Cl	23°	0.03g Cl		1	1ex	ac.595
$CoCl_2$	0.20 Cl	18°	0.03g Cl	1	1	1ex	c.596
	9.8	26°	0.16	½	2		ac.736 ± 0
	9.8	97°	0.13	½	2		ac.77– ± 2–
NaBr	0.39 Br	22°	0.05g Br		1	1ex	ac.625
KI	0.63 I	25°	0.1 g I		1	1ex	ac.505
HNO_3	0.32 HNO_3	25°	0.06g NO_3		1	1ex	ac.172
$NaNO_3$	0.33 NO_3	19°	0.02g NO_3		1	1ex	ac.629
Tl_2SO_4	0.25 SO_4	23°	0.03g SO_4		1	1ex	ac.528
$MgSO_4$	0.24 SO_4	24°	0.05g SO_4		1	1ex	ac.541
Na_2CO_3	0.16 CO_3	22°	0.014g CO_3		1	2ex	ac.590 ± 10
K_2CO_3	0.13 CO_3	23°	0.014g CO_3		1	1ex	ac.435 Pt/Pt.
NaOH	0.16 NaOH	25°	0.03g NaOH		1	1ex	ac.799 "
NH_4OH	0.18 NH_4OH	21°	0.014g NH_4OH		1	1ex	ac.562 "
$Ca(OH)_2$	0.11 $Ca(OH)_2$	24°	0.03g $Ca(OH)_2$		1	1ex	ac.786 "
$KMnO_4$	0.85 $KMnO_4$	23°	0.1g$KMnO_4$		1	1ex	ac.559 "
$H_2C_2O_4$	0.25 $H_2C_2O_4$	26°	0.04g $H_2C_2O_4$		1	1ex	c.214 "
Succinic Acid	0.59 S.Ac.	23°	0.04g S.Ac.		1	1ex	c.239 "

1898. H. Hoffmeister.

Ueber Stromleitung in gemischten Lösungen. Zeit. phys. Chem., *27*, 345.

Mixtures of from 1–9 parts of a solution of silver nitrate with 1–9 parts of a solution of nitric acid, and of 1–9 parts of sodium acetate with 1–9 parts of acetic acid, all four stock solutions being normal, were electrolyzed. The concentration changes for the cations of the nitrates were in accordance with that deduced by means of Rudolphi's dilution formula; for the sodium in the acetate mixture in accordance with Ostwald's dilution formula, while the acetic acid moved if at all toward the anode.

1898. K. Hopfgartner.

Ueber Stromleitung in gemischten Lösungen von Elektrolyten. Zeit. phys. Chem., *25*, 115.

For apparatus see Gordon, 1897; capacity 250 c.c. The Hg cathode was surrounded by a concentrated solution of $ZnCl_2$; for the electrolyses of sodium, hydrogen, and barium chlorides the anode was of Cd, for those with magnesium and cupric sulphates Cu was used. No diaphragms. The changes in the middle portions are listed in the fourth column below; 1g Ag in voltameter; method of calculation correct.

The paper also contains determinations of the transference in solutions of NaCl and HCl, $BaCl_2$ and HCl, $MgSO_4$ and $CuSO_4$, in widely different proportions, the concentrations varying from 0.1–1.0m per liter. The results are in accordance with those calculated from the conductivities of the salts taken separately, using Rudolphi's dilution formula.

NaCl	0.1m	16–17°	0.2–0.5 percent	3ex	a.617 ± 14
	0.2	13–19°	0.2–0.5 "	2	a.622 ± 1
	0.5	9–23°	0.2–0.5 "	3	a.623 ± 3
	0.8	13–19°	0.2–0.5 "	3	a.635 ± 2
	0.9	13–20°	0.2–0.5 "	3	a.635 ± 4
HCl	0.1m	15–18°	0.1–0.7 "	5ex	a.167 ± 20
	0.2	17–19°	0.0–0.5 "	4	a.164 ± 3
	0.5	13–26°	0.1–0.4 "	9	a.167 ± 18
	0.8	14–20°	0.1–0.3 "	6	a.157 ± 10
	0.9	13–20°	0.1 "	3	a.159 ± 10
$BaCl_2$	0.1m	14–18°	0.4–0.2 "	4ex	a.580 ± 13
	0.2	15°	0.4–0.2 "	2	a.592 ± 1
	0.5	11–15°	0.4–0.2 "	5	a.611 ± 16
	0.8	12–20°	0.4–0.2 "	5	a.617 ± 21
$MgSO_4$	1.0m	10–15°	0.4–0.2 "	3ex	a.749 ± 5
	1.3	10–13°	0.4–0.2 "	1	a.747
$CuSO_4$	1.0m	6–11°	0.1 "	3ex	a.696 ± 6
	0.7	8–15°	0.1 "	2	a.684 ± 7

1898. G. Kümmell.

Die Ueberführungszahlen von Zn- und Cd-Salzen in sehr verdünnten Lösungen. Wied. Ann., *64*, 655.

(i) The cathode vessel is attached to the top of the anode vessel by means of a side tube packed with cotton wool; capacity 175 c.c.; no change could be detected in the middle portion; Pt cathode; for Zn salts Zn anode, for Cd salts Cd anode; ap-

parently the incorrect method of calculation based on constant volume of solution was used.

$ZnCl_2$	0.01–0.003m	0.03g Zn	4ex	ac.603 ± 19
$ZnBr_2$	0.01–0.003m	0.02g Zn	3ex	ac.600 ± 12
ZnI_2	0.01–0.003m	0.02g Zn	3ex	ac.589 ± 12
$CdCl_2$	0.01–0.003m	0.05g Cd	3ex	ac.576 ± 8
$CdBr_4$	0.01–0.003m	0.05g Cd	3ex	ac.584 ± 9
CdI_2	0.01–0.003m	0.04g Cd	4ex	ac.552 ± 9
$ZnSO_4$	0.01–0.003m	0.03g Zn	4ex	ac.664 ± 7
$CdSO_4$	0.01–0.003m	0.04g Cd	4ex	ac.619 ± 15

(ii) By means of Helmholtz's formulæ, from the E.M.F. of concentration cells.

$ZnCl_2$	0.1–0.001m	4ex	.585 ± 3
$CdCl_2$	0.1–0.001m	4ex	.574 ± 10
$ZnSO_4$	0.025–0.001m	2ex	.587 ± 2
$CdSO_4$	0.025–0.001m	2ex	.627 ± 2

1898. D. McIntosh.

The Transference Number of Hydrogen. Jour. Phys. Chem., *2*, 273.

The transference number was obtained from the ratio of the E.M.F.'s of concentration cells with and without diffusion, making use of the formulæ of Helmholtz.

(i) Electrodes of hydrogen (platinised platinum), and mercury plus mercurous salt.

HCl	1.0–0.001m	6ex	.159 ± 3
HBr	"	6ex	.158 ± 6
HI	"	6ex	.161 ± 18
H_2SO_4	"	6ex	.174 ± 18
$H_2C_2O_4$	"	6ex	.163 ± 16

(ii) Electrodes of hydrogen and chlorine (platinised platinum).

HCl	1.0–0.1 m	1ex	.126
	1.0–0.01	1ex	.297
	0.1–0.01	1ex	.404

1898. O. Masson.

Ueber Ionengeschwindigkeiten. Zeit. phys. Chem., *29*, 501. Phil. Trans., 1899, *192*, 331.

Apparatus: two electrode chambers (flasks) connected by a narrow tube containing the gelatinized solution to be measured. "Indicators" were placed in the flasks (cupric sulphate or chloride at the anode, and potassium chromate at the cathode), and

the current passed until blue met yellow. Electrodes: Cu anode, Pt cathode; 18° C.

NH_4Cl	1.0m	18°	1ex	ac.490
KCl	0.5m		1ex	ac.495
	1.0		1ex	ac.490
	3		1ex	ac.483
NaCl	0.5m		1ex	ac.598
	1		1ex	ac.595
	2		1ex	ac.587
LiCl	0.5m		1ex	ac.687
	1		1ex	ac.680
K_2SO_4	0.5–1m		2ex	ac.467 ± 0
Na_2SO_4	1–0.5m		2ex	ac.567 ± 0
Li_2SO_4	2–0.5m		3ex	ac.658 ± 6
$MgSO_4$	2–0.5m		3ex	ac.693 ± 9

1898. R. Peters.

Ueber Oxydations und Reduktionsketten und den Einfluss komplexer Jonen auf ihre elektromotorische Kraft. Zeit. phys. Chem., *26*, 229.

Apparatus — a U-tube into both arms of which were dipped tubes closed at the lower end with parchment forming the anode and cathode compartments respectively, in the U-tube were plugs of cotton batting; Pt. electrodes; no middle portion.

The results are only qualitative, and show that in a solution of $FeFl_3.3NaFl + \frac{1}{2}H_2O$ containing 0.8 mg iron in 1 c.c. the iron moves toward the anode, presumably in the form of $FeFl_6'''$. In the case of an equivalent solution of $Fe_2(SO_4)_3$ under the same conditions the difference in titration value of a constant weight of solution before and after electrolysis was three times as great; here the iron moved towards the cathode.

1899. W. Bein.

Einige Versuche über die Abhängigkeit der Ueberführungen von Salzen von der Beschaffenheit der Membranen, welche die Elektroden-Lösungen voneinander trennen. Ein Beitrag zu dem Verhalten von Membranen gegen Salzlösungen. Zeit. phys. Chem., *28*, 439.

Apparatus: superposed glasses with diaphragms, viz.; earthenware (earth), fish bladder (fish b), parchment (parch), goldbeater's skin (gold). Capacity 200g; Pt electrodes in the experiments with CdCl. 20–22° C.

On page 447 of the paper is given a comparative table of

the results of Hittorf, Kuschel, Kirmis, and of the author, for the experiments in which diaphragms were used.

HCl	0.207 percent Cl	0.4 g Cl		earth	1ex	a.167
	0.207 " "	0.4		parch	1	a.176
	0.297 " "	0.4		fish b	1	a.29–
	0.208 " "	0.4		gold	1	c.29–
NaCl	0.20 " "	0.2 g Cl	0.05 percent	earth	2ex	ac.601 ± 1
	0.2–0.3 " "	0.3	2–3 "	fish	6	ac.718 ± 27
LiCl	0.27 " "	0.05g Cl	2–6 percent	gold	3ex	c.739 ± 17
$CaCl_2$	0.22 " "	0.03g Cl		earth	1ex	a.582
	0.22 " "	0.03		fish	4	a.733 ± 19
	0.22 " "	0.03		gold	2	a.805 ± 0
$CdCl_2$	0.20 " "	0.04g Cl	4 percent	fish	1ex	ac.763
	0.68 " "	0.06		earth	1	c.538

1899. W. Dittenberger und R. Dietz.

Ueber das elektrolytische Verhalten des Platin- und Zinnchlorids. Wied. Ann., *68*, 853.

Apparatus: (i) anode and cathode cylinders connected at the bottom by a tube of 0.5 mm. diameter bent seven times; (ii) and (iii) a similar tube bent three times (W-shaped). Capacity of (i) and (ii) 25–30g, of (iii) 300g; Pt electrodes; no diaphragms; no middle portion. The weight of Ag given below is calculated from the ampere-minutes. The solutions were analyzed only for Pt and Sn. The method of calculation is incorrect (constant volume of solution instead of constant amount of water). Although the conductivity greatly increases, the migration number is unaffected by setting the solution of $H_2.PtCl_4O$ in sunlight for 14 days.

$H_2.PtCl_4O$	0.50 m	0.002 g Ag	i	1ex	ac.137
	0.44	0.002	i	1	ac.132
	0.41	0.003	i	2	ac.125 ± 2
	0.36	0.003	i, ii	3	ac.125 ± 3
	0.10	0.0006	ii	2	ac.111 ± 2
	0.01	0.0006	iii	1	ac.077
	0.005	0.0003	iii	1	ac.075
$H_2.PtCl_6$	0.22 m	0.002 g Ag	i	1ex	ac.108
	0.007	0.0008	iii	1	ac.075
$SnCl_4$	6.6m	0.005 g Ag	i	1ex	ac.996
	1.2	0.002	i	2	ac.914 ± 13

1899. C. Dittrich.

Die Uranylsalze vom physikalisch-chemischen Standpunkt aus betrachtet. Zeit. phys. Chem., *29*, 481.

The solution to be investigated was placed in the bottom of a U-tube; above it in both branches was placed a solution of the pure acid, in some cases in tubes closed at the bottom with parchment, and containing Pt electrodes. When necessary the uranyl solution was made specifically heavier by the addition of urea. After the passage of the current the electrode solutions were examined for uranium. In the following table are given the components of the mixed solutions investigated, and the compartment into which the uranium migrated. All experiments were performed at least twice. In the cases of the pure uranyl salt solutions, the uranium was moved in all cases towards the cathode.

Na and UO_2 nitrates	cathode
" " " chlorides	"
" " " sulphates	"
" " " acetates (both concentrated)	anode
" " " " (" dilute)	cathode
" " " propionates	anode
" " " glycolates	cathode
" " " lactates	"
" " " oxalates	anode
" " " tartrates	"
" " " citrates	"
" " " salicylates	mostly cathode, partly anode.

1899. W. Hittorf und H. Salkowski.

Ueber eine merkwürdige Klasse unorganischer Säuren und ihr elektrolytisches Verhalten. Zeit. phys. Chem., *28*, 546.

Apparatus: two glass trays connected by a siphon, the cathode in a glass bell suspended above; capacity 25 c.c; Pt electrodes; no diaphragms; no middle portion; calculation correct.

$PtCl_4O.H_2$	7 percent	0.4g Ag	1ex	c.146
	2 "	0.1	1	c.126
$AuCl_3O.H_2$	24 percent	0.8g Ag	1ex	c.232
	12 "	0.5	1	c.233
	2 "	0.14	1	c.227

1899. O. Masson and B. D. Steele.

The Blue Salt of Fehling's Solution and other Cuprotartrates. Jour. Chem. Soc., *75*, 725.

Two flasks containing Pt electrodes surrounded by a neutral Fehling's solution, prepared by saturating a potassium hydroxide solution with cupric tartrate, were connected by a horizontal tube filled with a normal solution of sodium chloride solidified by gelatine. A blue color (complex anion) moved into the tube from the cathode but not from the anode side. In a second experiment where the anode vessel was filled with cupric sulphate solution, a dark blue color moved as before up the tube from the cathode flask, and a light blue (cupric chloride) from the anode end; before the latter met the dark blue its boundary was precipitated, showing that it had met a colorless anion (probably tartrate) which traveled faster than the complex copper-containing anion.

1899. M. Mugdan.

Zeit. f. Elektrochemie, *6*, 309 (see A. Kendrick, 1900).

1899. W. Starck.

Neue Beiträge zur Kenntnis der Ionen verdünnter Schwefelsaure. Zeit. phys. Chem., *29*, 385. Auszug aus einer Greifswalder Dissert.

Apparatus: (i) superposed glasses with parchment or earthenware diaphragms. (ii) three U-tubes connected by two siphons; no diaphragms; capacity 30–40 c.c. Middle portions unchanged; Pt electrodes; method of calculation correct. "Diaphragms hold the cation"; Cf. Bein, "hold anions."

H_2SO_4	0.30	percent	17–20°	0.2g Ag	i	Iex	a.135
	0.5–0.6	"	17–20°	0.3	i	5	a.145 ± 7
	2.6	"	17–20°	0.9	i	1	a.163
	5.2	"	17–20°	1.1	i	1	a.175
	10–18	"	17–20°	1.1	i	7	a.195 ± 13
	30.4	"	27–20°	1.1	i	4	a.215 ± 8
	0.59	"	31°	0.4	ii	1	ac.204
	5.5	"	16°	0.6	ii	1	ac.198
	5.5	"	7°	0.6	ii	1	ac.191
	39.6	"	5°	1.1	ii	2	ac.218 ± 3
	42.0	"	35–37°	0.9	ii	4	ac.277 ± 10
	50.5	"	36°	0.9	ii	1	ac.450
	62.0	"	15°	0.7	ii	1	ac.497
	70.2	"	29°	0.9	ii	1	ac.569
	70.1	"	47°	0.8	ii	1	ac.709
	81.0	"	16°	0.8	ii	2	ac.644 ± 4

1900. K. Hellwig.

Ueber einige komplexe Silbersalze. Zeit. anorg. Chem., *25*, 157.

Apparatus U-shaped, consisting of two vertical tubes connected underneath by a narrow tube with a glass tap in the middle; Ag electrodes surrounded with cotton. The author showed by qualitative experiments that AgI moves toward the cathode, probably as component of a complex cation, in solutions of $Ag_3I(NO_3)_2$ containing from 0.2g AgI in 10 c.c. up to saturation (the latter at 70° C.).

1900. A. Kendrick.

Ueberführungszahl von Schwefelsäuregemischen aus Messungen am Bleiakkumulator. Zeit. f. Elektrochemie, 7, 52.

The author measured the E.M.F.'s of three types of concentration cell; in each, electrodes of the same material were immersed in two solutions of sulphuric acid, which were connected by a siphon; the three kinds of electrodes used were Pb, H_2 and PbO_2. The migration value was calculated from the formulæ for the E.M.F.'s of each two sorts; the headings of the columns below indicate which two were used as the basis of calculation.

		H_2 and PbO	H_2 and Pb.
H_2SO_4	1.8 percent	.147	.189
	2.5 "	.213	.218
	4.0 "	.188	.228
	5.0 "	.178	.207
	7.5 "	.164	.188
	10.0 "	.156	.181
	12.5 "	.131	.158
	15.0 "	.140	.162
	17.5 "	.131	.168
	20.0 "	.132	.177
	22.5 "	.133	.177
	25.0 "	.144	.197
	27.5 "	.187	
	30.0 "	.217	
	32.5 "	.263	
	35.0 "	.284	
	37.5 "	.296	
	40.0 "	.327	
	42.5 "	.349	
	45.0 "	.351	
	47.5 "	.359	
	50.0 "	.396	
	52.5 "	.420	
	55.0 "	.456	

The values calculated from Pb and PbO_2 electrode cells are supplemented by corresponding values calculated from the measurements of Mugdan (1899, Zeit. f. Electrochemie, *6*, 316) which are given in the third column below.

	Pb and PbO_2.	Mugdan.
1.4 percent	.180	.300
2.7 "	.200	.290
5.3 "	.100	.258
10.2 "	.144	.245
19.4 "	.216	.282

1901. H. T. Calvert.

Ueber die Alkalisalze des Hydroperoxyds in wässriger Lösung. Zeit. phys. Chem., *38*, 535. Zeit. f. Elektrochem., *7*, 624.

In the bottom of a U-tube was placed the solidified solution obtained by diluting a saturated potassium nitrate solution sevenfold with 2 percent agar agar solution and adding 8 percent (volume) of a normal sodium hydroxide solution which had been saturated with lead oxide. Above this on both sides of the U-tube was placed a layer 1 cm. deep of the same solution without the addition of plumbite. The rest of the tube was filled with a solution $\frac{1}{4}$ m. in respect to NaOH, 1.0 m. in respect to H_2O_2. The specific conductivity was the same throughout the tube, the temperature was 0° C. On passing a current through, a brown ring of lead superoxide was formed in the *lower* agar agar solution at the boundary on the cathode side, and another in the aqueous solution at the boundary on the anode side. Reversing the current reversed the phenomena. Although the author does not discuss the possibility of cataphoresis the resultant difference of 2 cm. in hydrostatic level on the two sides (which would be necessary to explain the results on this supposition) could not escape observation, and thus the experiment demonstrates the migration of a peroxide ion.

1901. R. Gans.

Ueber die Abhängigkeit der elektrolytischen Ueberführung und der elektromotorischen Kraft reversibler Elemente von physikalischen Einflüssen. Drude's Ann., *6*, 315.

From his measurements of the E.M.F. of the concentration cell Zn/0.4 m. $ZnSO_4$/0.04 m. $ZnSO_4$/Zn the author deduces the formula $n = 0.699\ (1 + 0.00012\ p)$ to represent the effect of

pressure upon the migration value, which he assumes as 0.699; $\not{p}$ is the pressure in atmospheres.

1901. H. Jahn's Schüler.

Ueber die Wanderungsgeschwindigkeit der Ionen in verdünnten Lösungen. Zeit. phys. Chem., *37*, 673; *38*, 127.

Apparatus: N-shaped tube fitting on top of the Erlenmeyer-flask-like anode compartment; capacity of the anode vessel 300–700 c.c.; no diaphragms; Hg cathode surrounded by a concentrated solution of copper nitrate or cadmium sulphate; 18°–19°; calculation correct.

In the fourth column I have calculated the percent change in the middle portion.

			Percent.				
Bogdan.							
HCl	0.031–0.0091m	0.4g Ag	0.1	17ex	a .174 ± 6	Zn	anode
Bukschnewski.							
HNO_3	0.25–0.0066m	0.2–4g Ag	0.1–0.01	23ex	a .170 ± 4	Ag	"
Bogdan.							
KCl	0.03–0.008m	0.4g Ag	0.1	11ex	a .503 ± 2	Zn	"
NaCl	0.03–0.008m	0.4g Ag	0.03–0.1	12ex	a .604 ± 2	"	"
KBr	0.03–0.01m	0.4g Ag	0.03	9ex	a .504 ± 2	"	"
	0.069–0.034	0.5	0.1	6	a .500 ± 2	"	" [1]
	0.017–0.011	0.2	0.13	4	a .495 ± 3	"	" [1]
	0.066	0.3	0.07	3	a .494 ± 2	"	" [2]
	0.3	0.3	0.2	3	a .503 ± 2	"	" [2]
NaBr	0.015–0.006m	0.2g Ag	0.2–0.02	6ex	a .604 ± 3	"	"
Oppenheimer.							
NaBr	0.032–0.006m	0.4g Ag	0.06–0.01	15ex	a .606 ± 2	"	"
Goldhaber.							
LiCl	0.253m	0.7g Ag	0.1	3ex	a .700 ± 2	"	"
	0.125	0.8	0.1	3	a .688 ± 3	"	"
	0.0624	0.5	0.1	3	a .684 ± 2	"	"
	0.03–0.008	0.4	0.1–0.01	18	a .669 ± 5	"	"
Berliner.							
$AgNO_3$	0.03–0.005m	0.3g Ag	0.1–0.03	13ex	a .530 ± 5	"	"
Bukschnewski.							
$BaCl_2$	0.016m	0.5g Ag	0.1–0.01	3ex	a .543 ± 1	"	"
	0.008	0.4	0.1–0.03	3	a .548 ± 2	"	"
	0.0056–0.0029	0.3	0.1–0.01	9	a .553 ± 2	"	"

[1] 25 percent ethyl alcohol.
[2] 50 percent ethyl alcohol.

Goldhaber.							
$CdCl_2$	0.06–0.008m	0.8g Ag	0.4–0.01	23ex	a .570 ± 3	Cd	anode
Bukschnewski.							
$CdCl_2$	0.006–0.0032m	0.3g Ag	0.07–0.01	9ex	a .570 ± 2	"	"
Goldhaber.							
$CdBr_2$	0.502m	1.2g Ag	0.1	3ex	a .782 ± 2	"	"
	0.251	0.8	0.1	3	a .650 ± 3	"	"
	0.125	0.7	0.1	3	a .601 ± 2	"	"
	0.083	0.8	0.1	3	a .577 ± 2	"	"
	0.06–0.01	0.4	0.3–0.01	21	a .569 ± 4	"	"
Bukschnewski.							
$CdBr_2$	0.008–0.0033m	0.3g Ag	0.1–0.01	12ex	a .571 ± 4	"	"
Redlich.							
CdI_2	0.249m	1 g Ag	0.2–0.0	3ex	a1.003 ± 16	"	"
	0.125	1 g Ag	0.2–0.0	3	a .925 ± 9	"	"
	0.0805	1 g Ag	0.2–0.0	2	a .777 ± 12	"	"
	0.0623	1 g Ag	0.2–0.0	3	a .719 ± 7	"	"
	0.0409	1 g Ag	0.2–0.0	2	a .657 ± 1	"	"
	0.0311	1 g Ag	0.2–0.0	3	a .619 ± 6	"	"
	0.0207	1 g Ag	0.2–0.0	3	a .593 ± 1	"	"
	0.0140	0.6g	0.2–0.0	3	a .573 ± 2	"	"
	0.0124	0.6	0.2–0.0	3	a .558 ± 2	"	"
	0.01	0.6	0.2–0.0	3	a .554 ± 4	"	"
Bukschnewski.							
CdI_2	0.0163m	0.3g Ag	0.1–0.00	3ex	a .578 ± 2	"	"
	0.008–0.003	0.2	0.1–0.00	10	a .557 ± 2	"	"
Redlich.							
$CdSO_4$	1.00m	1.6g Ag		3ex	a .746 ± 7	"	"
	0.50	0.9		3	a .706 ± 13	"	"
	0.251	0.9		4	a .677 ± 6	"	"
	0.125	0.9		3	a .659 ± 2	"	"
	0.0836	0.7	0.1	3	a .646 ± 4	"	"
	0.0628	0.6		2	a .638 ± 5	"	"
	0.0416	0.6	0.05	3	a .632 ± 5	"	"
	0.0312	1.1	0.07	3	a .628 ± 3	"	"
	0.0208	1.1	0.00	3	a .621 ± 3	"	"
Metelka.							
$CuSO_4$	0.25–0.12m	0.9g Ag	0.1	6ex	a .672 ± 9	Cu	"
	0.0820	0.9	0.2	3	a .634 ± 5	"	"
	0.0625	0.9	0.3	3	a .627 ± 2	"	"
	0.0416	0.9	0.2	3	a .626 ± 0	"	"
	0.03–0.01	0.9	0.4–0.1	15	a .625 ± 3	"	"

1901. W. Kistiakowsky.

Electrochemistry of Double Salts. Jour. Chem. Soc., *82*, II, 121; Zeit. f. Elektrochem., *8*, 71 (from Jour. Russ. Phys. Chem. Ges., *33*, 480, 592).

For apparatus see Kistiakowsky, 1890. From the author's measurements of $Ag_3Cr(C_2O_4)_3$, $K_4Fe(CN)_6$ and $K_3Co(CN)_6$ he concludes that the complex ions obey Kohlrausch's Law. Data are not quoted in the reviews.

1901. A. A. Noyes.

A Modification of the Usual Method of Determining Transference Numbers and an Investigation of the Influence of the Concentration on Their Values in the Case of Some Tri-Ionic Salts. Zeit. phys. Chem., *36*, 63. Jour. Am. Chem. Soc., *23*, 36. Phys. Rev., *12*, 15.

Apparatus: a pair of vertical U-tubes connected by a horizontal piece; capacity 1050 c.c.; Pt electrodes; no diaphragms. The solutions were kept neutral at the electrodes by adding acid and alkali during the electrolysis. The electrolyses were carried out at 25° C. In the fourth column are given the changes in the middle portions. The method of calculation is correct.

K_2SO_4	0.1m	3g Ag	0.3–0.03 percent	3ex	c.5069 ± 1.1
	0.02	0.5	0.3–0.03 "	3	c.5038 ± 0.5
$BaCl_2$	0.1m	2g Ag	0.1–0.05 "	4ex	c.5853 ± 0.3
	0.02	0.5	0.1–0.02 "	3	c.5578 ± 0.8
$Ba(NO_3)_2$	0.2m	2g Ag	0.02–0.01 "	4ex	ac.5450 ± 0.7
	0.04	0.5	0.003–0.00 "	3	ac.5437 ± 2.2

1901. A. A. Noyes and A. A. Blanchard.

Vorlesungsversuche zur Veranschaulichung der elektrolytischen Dissociation, der Gesetze des Gleichgewichts, und der Geschwindigkeit chemischer Vorgänge. Zeit. phys. Chem., *36*, 1.

Lecture experiments Nos. 5, 6, and 7 employ rather complex mixtures to show qualitatively by the direct method the migration of the ions of copper chromate, potassium hydrate, a mixture of hydrochloric acid and cupric chloride, and of potassium silver cyanide.

1901. W. Pfanhauser.

Ueber das elektrochemisches Verhalten des Nickelammonsulphats. Zeit. f. Elektrochemie, 7, 698.

Apparatus: a U-tube with a glass vessel upon each end; Ni anode surrounded by a solution of ammonium sulphate; Pt cathode; parchment diaphragms.

$(NH_4)_2.Ni(SO_4)_2$ saturated solution		18° C	.507	
	0.1m	18°	Ni .118 / NH_4 .272	toward cathode.
	0.7m	50°	.499	

1901. E. Rieger.

Ueber die Konstitution halbkomplexer Salze nach ihrer elektrolytischen Ueberführung. Dissert. Breslau. Zeit. f. Elektrochemie, 7, 863, 871.

Apparatus: two vertical U-tubes joined by a sloping tube (capacity 60 c.c.); Pt. electrodes; no diaphragms; 0.4g Ag; middle portions unchanged.

The results below were calculated by the author for concentration changes in constant volume, not for constant amounts of water, as is correct. A Cu anode was employed in the experiments with copper sulphate, and an Ag anode with potassium mercury cyanide.

Lest the experimental results of this paper presented in a short summary should be misleading, I have introduced the fifth column below which records the number of monovalent equivalents moved from the cathode into the anode compartment while one equivalent of silver is precipitated in the voltameter; in the case of $K_2SO_4.CuSO_4$, the Cu moved toward the cathode. The sixth column gives Rieger's interpretation of the results.

In experiments with potassium ferrous oxalate the author found a small increase in the concentration of Fe at the anode.

$CuSO_4$	0.291m	5ex		a.67- ± 15
$CuSO_4.K_2SO_4$	0.291m	5	—0.071 Cu	
	0.191m	3	—0.074 Cu	
AgI 0.078m + KI 1.96 m		4ex	0.018 Ag	
HgI_2 0.214m + KI 0.782m		5ex	0.26 Hg	
$Hg(CN)_2.2KCN$ 0.810m		4ex	0.34 Hg	$Hg(CN)_4$ a.34- ± 10
$Zn(CN)_2$ 0.281m + KCN 1.087m		3ex	0.22 Zn	
$Cd(CN)_2.2KCN$	0.772m	5ex	0.30 Cd	$Cd(CN)_4$ a.29- ± 20
$K_3Fe(C_2O_4)_3$	0.408m	5ex	0.43 Fe	$Fe(C_2O_4)_3$ a.43- ± 20

1901. E. H. Riesenfeld.

Ueber elektrolytische Erscheinungen an der Grenzfläche zweier Lösungsmittel. Zeit. f. Elektrochem., 7, 645.

An entirely new method. An electrolyte is dissolved in two not completely miscible solvents so that these are in equilibrium

with each other, and the two solutions are placed in a U-tube so that there is a layer of the lighter solution in both arms surrounding the electrodes while the heavier fills the bottom of the tube. If now an electrochemical equivalent of current be sent through, there will have occurred in the one meniscus an increase of concentration, in the other a decrease, both equal to the difference in migration value in the two solvents. This accumulation in the boundary is divided between the surface layers of the two liquids in the relation of the distribution ratio (Verteilungscoefficient), and is removed from them in proportion to the rates of diffusion in the two solvents. Hence in a favorable case where the product of the distribution ratio and the square root of the ratio of the rates of diffusion is large, practically all the accumulated electrolyte goes into the electrode solution. Hence from analysis of the electrode solution before and after electrolysis we may measure the migration value in the solvent in the middle of the tube. The fact that with potassium iodide the value, 19– was obtained under variation of the concentration (from 0.029 m to 0.13 m in the aqueous solution), the volume of electrode solution, and the current density is regarded as a proof of the correctness of the theoretical treatment. For potassium dichromate, ferric sulphocyanate, and ortho-nitro-phenol the migration value of the anion is greater than in aqueous solution.

1901. **B. D. Steele.**

A New Method for the Measurement of Ionic Velocities in Aqueous Solution. Trans. Chem. Soc., *79*, 414. Zeit. f. Elektrochem, *7*, 618.

Apparatus: an H-tube with electrode chambers attached. The H-tube contained the aqueous solution to be investigated; while the electrode chambers were filled with an "indicator" solution solidified by gelatine. The author measured the ratio between the rates at which the tube's two surfaces of contact approached each other; the boundaries being detected by the difference in refraction. The indicators employed had one ion in common with the solution to be measured, while the specific velocity of the other ion was less than that of the ion it followed through the H-tube. Under these conditions the observed rates are proportional to the specific ionic velocities.

Two determinations with $MgSO_4$ in 2 m solution by the analytical (Hittorf) method are published without data; $n = .732$ and .744.

The third column in the table below gives the indicators employed. "Most of the experiments were carried out at 14° C." No allowance was made for cataphoresis.

$MgSO_4$	2.0m	$CuSO_4$, K_2CrO_4		ac.729
	2.0m	" "		ac.688 (in gelatine)
	2.0m	" $NaC_2H_3O_2$		ac.734
	2.0m	$CdSO_4$, "		ac.738
	2.0m	LiCl, "		ac.56– to .61–
NaCl	2.0m	" "		ac.590
	1.0	" "		ac.592
	0.5	" "		ac.597
KCl	2.0m	" "	6ex	ac.489
	1.0	" "		ac.488
	0.5	" "		ac.490
KBr	2.0m	" "	6ex	ac.468
	1.0	" "	2	ac.473
	0.5	" "	5	ac.478
	0.1	" "		ac.483
NaBr	0.5m	" "		ac.595
$CdSO_4$	2.0m	" "		ac.62– to .65–

1901. A. Wiesler.

Beiträge zur Kenntnis der Metaphosphate. Zeit. anorg. Chem., *28*, 190.

Apparatus same as used by Jahn, capacity of anode 200 c.c.; Zn anode, Hg cathode; no diaphragms; method of calculation correct.

$NaPO_3$	0.039m	0.65g Ag	1 percent	2ex	a.590 ± 0

1902. R. Abegg und W. Gaus.

Beiträge zur Theorie der direkten Bestimmungsmethode von Ionenbeweglichkeiten. Zeit. phys. Chem., *40*, 737.

The apparatus and method were the same in principle as those used by Steele, 1901 and 1902, but modified to measure the cataphoresis.

NaCl	3 percent	LiCl, $NaC_2H_3O_2$	7ex	ac.606 varied potential fall.
KCl	0.5m ?	" "	1ex	ac.508 corrected for cataphoresis.

1902. A. Coehn.

Ein Beitrag zur Oxoniumtheorie. Ber. *35*, III, 2673.

The author showed that when a solution of 20 percent hydrochloric acid and 20 percent di-methyl-pyrone is placed between electrode solutions of 10–20 percent hydrochloric acid, that the

di-methyl-pyrone moves into the cathode compartment. The first apparatus was a beaker into which dipped tubes closed underneath with parchment and containing the electrodes and hydrochloric acid. The second was a vertical U-tube, the upper halves of whose arms were attached by ground glass joints so that they could be separated by sliding horizontally; the lower half contained the di-methyl-pyrone.

1902. F. G. Donnan, H. B. Bassett and C. J. J. Fox.

The Color Changes exhibited by the Chlorides of Cobalt and some other Metals, from the standpoint of the Theory of Electroaffinity. Jour. Chem. Soc., *81*, 939.

Two electrode chambers are connected by a horizontal tube closed at each end by a plug of plaster of Paris. When the electrode compartments were filled with strong solution of calcium chloride and blue cobalt chloride, and the horizontal tube with calcium chloride solution, the blue color traveled down the tube toward the anode. When the end vessels contained red cobalt chloride and the tube potassium chloride, the red color moved toward the cathode. Cataphoresis was not measurable. Further experiments were performed in a U-tube, the lower half containing the heavy solution, and both arms the other (electrode) solution.

	Lower Colored Layer.	Upper Colorless Layer.
(1)	$CoCl_2$ (blue) in concentrated HCl	concentrated HCl
(2)	" " " " $MgCl_2$	" $MgCl_2$
(3)	" " " " $CaCl_2$	" $CaCl_2$
(4)	fairly dilute $CoCl_2$ (red)	KCl
(5)	$CoCl_2$ (red) + concentrated $CaCl_2$ and $ZnCl_2$	concentrated $CaCl_2 + ZnCl_2$
(6)	Fehling's solution	alkaline tartrate solution
(7)	ammoniacal copper sulphate	$NH_4OH + NH_4SO_4$
(8)	$CoCl_2$ (blue) in alcohol	$CaCl_2$ or HCl in alcohol
(8*a*)	$CoCl_2$ (red) in alcohol at —79°	$CaCl_2$ or HCl in alcohol
(9)	$CoCl_2$ (red) + $HgCl_2$ in alcohol	$HgCl_2$
(10)	" " " " " "	HCl
(11)	$FeCl_3$ in concentrated HCl	(concentrated HCl) ?
(12)	$CuCl_2$ " " "	" "

In (1), (2), (3), (6), (8), the blue color moved toward the anode; in (4), (5), (7), (9) and (8*a*) the red color moved towards the cathode; in (10) the blue meniscus on the anode side moved off toward the anode leaving a colorless layer above the red solution, at the cathode side the blue color at the meniscus ex-

tended itself down into the red layer, although the meniscus remained stationary; in (11) and (12) the brownish yellow moved toward the anode.

The foregoing experiments, the general behavior, the freezing points and conductivity alone and mixed, etc., are all consistently explained by the authors' conclusion that the simple cobalt cation is red, and that the blue is a complex anion $CoCl_3'$ or $CoCl_4''$. Similarly the brownish yellow of ferric and copper chlorides is attributed to a complex anion.

1902. W. Hittorf.

Bemerkungen über die Bestimmungen der Ueberführungszahlen der Ionen während der Elektrolyse ihrer Lösungen. Das Verhalten der Diaphragmen bei derselben. Arch. Neerl. (2) *6*, 671; Zeit. phys. Chem., *39*, 613; *43*, 239. Drude's Ann., *9*, 243.

Apparatus: N-shaped tubes and superposed glasses; capacity of anode vessel 20–40g; no middle portion. Various diaphragms were employed, viz.: bolting silk (bolt), earthenware (earth), intestinal membrane (darm) and gold beaters' skin (gold). Anode Cd, the cathode is indicated below in the fourth column. One experiment each.

The author observed with a differential spectroscope the currents occasioned in the solutions by the diaphragms; these occurred only with the chlorides of cadmium, calcium, barium, and strontium, the nitrates of silver and thallium, and the strong free acids; not with the nitrates, acetates, and iodides of the alkalis. The action is described as the splitting up of the solution into a more concentrated and a more dilute, which are ejected at opposite sides of the diaphragm. The diaphragms which modify the transport number are: intestinal membrane, gold-beaters' skin, membrane of an egg, and gelatine. Without influence are: agar agar, and earthenware.

$CuSO_4$	0.656 m	16°	1.1g Ag	Hg	darm	a .714
$BaCl_2$	0.125 m	25°	0.8g Ag	Pt	bolt	a .644
	0.125	25°	1.0	"	earth	a .648
	0.0908	23°	0.3	"	bolt	a .576
	0.0908	23°	0.3	"	bolt, earth	a .575
$CaCl_2$	0.123 m	20°	0.7g Ag	"	bolt	a .675
	0.0551	20°	0.2	"	earth	a .596
$MgCl_2$	1.40 m	23°	0.5g Ag	"	bolt	a .719
	0.104	24°	0.2	"	"	a .649

$CdCl_2$	7.69 m	22°	1.4g Ag	Hg	none	a1.137
	2.61	19°	0.7	"	"	a .801
	1.33	19°	1.5	"	"	a .724
	0.372	17°	0.8	"	"	a .589
CdI_2	1.61 m	17°	0.5g Ag	"	"	a1.245
$ZnCl_2$	3.56 m	18°	1.0g Ag	"	"	a1.241
$CdCl_2$	0.101 m	17°	0.3g Ag	"	"	a .565
	0.101	17°	0.3	"	earth	a .568
	0.101	17°	0.3	"	darm	a .743
	0.101	16°	0.2	"	darm, earth	a .564
	0.0704	22°	0.5	"	darm	a .737
	0.0965	17°	0.3	"	"	a .593
	2.70	19°	0.5	"	"	a .844
	1.57	17.5°	0.5	"	gold	a .802
	1.49	18°	0.4	"	"	a .801
	0.0404	19°	0.2	"	"	a .752
	0.0131	18.9°	0.1	"	"	a .636
	0.11		0.5	"	solidified by gelatine	a .551
KCl	0.226 m	17°	0.4g Ag	Pt	darm	a .509

1902. H. Morse.

Ueber die Dissociation der Merkurihaloide. Zeit. phys. Chem., *41*, 709.

By qualitative measurements it was found that when the following chemicals are dissolved in strongly acid mercuric nitrate solutions and electrolysed, the halogen increases in concentration in the cathode solution: AgCl, $HgCl_2$, AgBr, $HgBr_2$, AgI, HgI_2; the property increasing in the order mentioned. The preliminary experiments were performed in a U-tube, the solution being solidified with agar agar and the upper half of the tube being filled with silver nitrate; cataphoresis was pronounced. The final experiments were made in two beakers connected by a siphon without diaphragms.

1902. A. A. Noyes and G. V. Sammet.

The Equivalent Conductivity of the Hydrogen Ion derived from Transference Experiments with Hydrochloric Acid. Jour. Am. Chem. Soc., *24*, 944. Zeit. phys. Chem, *43*, 49.

Apparatus: a pair of vertical U-tubes connected by a horizontal piece; capacity 1300 c.c.; Pt electrodes; no diaphragms; calculation correct.

The paper further contains measurements of the conductivity of the hydrochloric acid.

In the following table the results discarded by the authors are omitted.

HCl	0.050 m	20°	0.8g Ag	0.6–0.00	percent	9ex	ac.1657 ± 2.3
	0.017	20°	0.3	0.5–0.00	"	11	ac.1674 ± 1.9
	0.017	10°	0.3	0.1–0.00	"	6	ac.1586 ± 1.3
	0.017	30°	0.3	0.6–0.00	"	6	ac.1773 ± 0.6
	0.0056	20°	0.18	0.2	"	10	ac.1671 ± 2.7

1902. E. H. Riesenfeld.

Bestimmung der Ueberführungszahl einiger Salze im Phenol. Drude's Ann., *8*, 609.

For apparatus and method see Riesenfeld, 1901 ; Pt electrodes.

KI	0.03–0.2 m	13°–20°	0.2 g Ag	c.191
KBr	0.134 m	14°	0.27g Ag	c.196
KCl	0.212 m	15°–16°	0.3 g Ag	c.192
LiCl	0.167 m	15°	0.25g Ag	c.229

1902. H. Schlundt.

On the Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile. Jour. Phys. Chem., *6*, 159.

Apparatus: similar to a Gay-Lussac's burette, Ag cathode at top, Ag anode at bottom; capacity 30 c.c. and 60 c.c.; no diaphragm; middle portion changed less than 1 percent; method of calculation correct.

$AgNO_3$ in Pyridine				
1.0 m	23°	0.17g Ag	1ex	ac.673 ± 1
0.5	0°–23°	0.16	3	ac.661 ± 4
0.1	0°–21°	0.16	3	ac.603 ± 9
0.025	22°	0.05	2	ac.559 ± 8
$AgNO_3$ in Acetonitrile				
1.0 m	18°	0.2 g Ag	1ex	ac.616 ± 2
0.275	19°	0.12	1	ac.578 ± 2
0.091	17°	0.12	1	ac.551 ± 4
0.029	19°	0.08	1	ac.529 ± 2

1902. B. D. Steele.

Die Messung von Ionengeschwindigkeiten in wässerigen Lösungen, und die Existenz komplexer Ionen. Zeit. phys. Chem., *40*, 689. Phil. Trans., *198*, 105. Jour. Chem. Soc., *79*, 414.

For apparatus and method, see Steele, 1901. The indicators (normal solutions) were $CuSO_4$ with Cu anode, $LiCl + Li_2CO_3$, $MgCl_2 + MgO$, $CdSO_4$ with Cd anode, $Na.C_2H_3O_2 + H.C_2H_3O_2$, $KF + H.C_2H_3O_2$.

Observations made at the indicator boundaries showed the existence of complex anions in solutions of KI_3 and $KFe'''Ox$.

KCl	0.5–2.0 m	LiCl,	$NaC_2H_3O_2$	ac.489 ± 1
NaCl	0.5 m	"	"	ac.597
	1.0	"	"	ac.591
	2.0	"	"	ac.590

KBr	0.1 m	LiCl, $NaC_2H_3O_2$	ac.483
	0.5	" "	ac.478
	1.0	" "	ac.473
	2.0	" "	ac.468
$KBrO_3$	0.29 m	" "	ac.385
NaBr	0.5 m	" "	ac.595
LiCl	0.5 m	$CdSO_4$, "	ac.716
	1.0	" "	ac.751
KOH	0.574 m	LiCl, KBr	ac.730
$AgNO_3$	1.15 m	$CuSO_4$, KFl	ac.486
$BaCl_2$	0.25 m	$MgCl_2$, $NaC_2H_3O_2$	ac.576
	0.5	" "	ac.619
	1.0	" "	ac.633
$SrCl_2$	0.25 m	" "	ac.625
	0.5	" "	ac.665
	1.0	$CuSO_4$ "	ac.709
$CaCl_2$	0.25 m	$CdSO_4$ "	ac.681
	0.5	" "	ac.697
	1.0	$CuSO_4$ "	ac.715
$MgCl_2$	0.25 m	$CdSO_4$, "	ac.705
	0.5	" "	ac.722
	1.0	$CuSO_4$ "	ac.740
$MgSO_4$	0.092 m	$CdSO_4$ "	ac.646
	0.25	" "	ac.693
	0.5	" "	ac.715
	1.0	" "	ac.737
$CuSO_4$	0.5 m	" "	ac.66–
	1.0	" "	ac.73–
K_2CrO_4	0.25 m	LiCl "	ac.447
	1.0	" "	ac.403
KFe'''Ox	0.603 m	" "	ac.331

1902. B. D. Steele and R. B. Denison.

The Transport Number of very Dilute Solutions. Trans. Chem. Soc., *81*, 456.

Apparatus: a W-tube arranged so that a current of unaltered solution could be passed down through the inside legs, so that the middle portion was continually renewed; this made the total quantity of liquid for analysis in each half of the apparatus three liters; no diaphragms; Pt electrodes surrounded with alkali and acid respectively; calculation correct.

$CaSO_4$	0.0045 m	0.3g Ag	0.4–2 percent	6ex	c.559 ± 13
$Ca(NO_3)_2$	0.0047 m	0.4g Ag	2–0.4 "	3ex	c.550 ± 3
$CaCl_2$	0.0046 m	0.4g Ag	2–0.3 "	3ex	c.562 ± 6
KCl	0.0025–0.0046m	0.4g Ag	1–0.06 "	9ex	c.505 ± 4

Proc. Wash. Acad. Sci., June, 1907.

1903. **G. Carrara.**

Per la teoria della dissociazione elettrolitica in solventi diversi dall'acqua. III. Influenza del solvente sopra i numeri di trasporto. Gazz. chim. *33*, I, 241.

Apparatus: (i) see Loeb and Nernst; capacity 30 c.c.; (ii) cylindrical glasses superposed on one branch of a U-tube, the bottom of each being closed by fish bladder; capacity 40–70 c.c.; (iii) an M-tube without diaphragms with outlets on the three lower extremities; capacity 100 c.c.; two middle portions with a change 2–20 percent as great as the end portions; 25°C. The method of calculation is correct. The unusual duration of the experiments (up to 50 hours) must have occasioned mixing by diffusion and convection. The solvent was in all cases pure methyl alcohol.

				Anode. Cathode.		
$AgNO_3$	0.0093 m	0.03g Ag	i	Ag/Pt	3ex	ac .489 ± 23
$Cu(NO_3)_2$	0.125 m	0.2 g Ag	i	Cu/Pt	3ex	a .454 ± 9 c .375 ± 70
	0.111	0.2	i	"	4	a .491 ± 18 c .285 ± 68
$Cd(NO_3)_2$	0.02–0.05 m	0.7 g Ag	i	Cd/Pt	3ex	ac .430 ± 10
$LiNO_3$	0.260 m	0.8 g Ag	i	"	1ex	ac .765 ± 6
	0.260	0.7	ii	"	2	ac .753 ± 20
	0.21	0.7	ii	Pt or Cd/Pt	2	ac .710 ± 37
$AgClO_3$	0.0118 m	0.03g Ag	i	Ag/Pt	3ex	a .418 ± 4 c .377 ± 10
$Cu(ClO_3)_2$	0.114 m	0.4 g Ag	i	Cu/Pt	3ex	a .580 ± 14 c .42– ± 65
$LiClO_3$	0.19 m	0.6 g Ag	i[1]	"	1ex	ac .707 ± 11
	0.14	0.4	i[1]	Cu or Pt/Pt	2	ac .719 ± 15
$Cd(ClO_3)_2$	0.083 m	0.5 g Ag	i	Cd/Pt	2ex	ac .273 ± 8
	0.024	0.15	i	"	2	ac .223 ± 9
$CuCl_2$	0.189 m	0.6 g Ag	iii	Cu/Pt	1ex	ac .642 ± 0
	0.062	0.25	iii	"	1	ac .629 ± 5
$CdCl_2$	0.0558 m	0.1 g Ag	iii	Cd/Pt	2ex	ac .736 ± 10
	0.0380	0.14	iii	"	1	ac .627 ± 21
	0.0254	0.04	iii	"	2	ac .608 ± 6
CdI_2	0.1060 m	0.1 g Ag	i	"	2ex	ac 1.409 ± 1
	0.0532	0.1	i	"	2	ac 1.270 ± 17
	0.0243	0.05	i	"	2	ac 1.211 ± 19
LiI	0.02–0.1 m	0.3 g Ag	ii	"	3ex	ac .632 ± 21
	0.057	0.16	iii	"	1	ac .590 ± 9
$N(C_2H_5)_4.I$	0.048 m	0.03g Ag	ii	"	1ex	ac .764 ± 3
	0.0260	0.09	iii	"	1	ac .730 ± 0
$S(CH_3)_3.I$	0.091 m	0.17g Ag	iii	"	1ex	a .623 c .568

[1] With fish-bladder diaphragms.

$Cd.(C_2H_3O_2)_2$	0.0515 m	0.1 g Ag	i	"	2ex	ac .240 ± 8
	0.0275	0.1	i	"	1	ac .167 ± 2
$Cu.(C_2H_3O_2)_2$	0.0174 m	0.08g Ag	ii	Cu/Pt	2ex	c .594 ± 29
$Li.C_2H_3O_2$	0.29 m	0.6 g Ag	ii	Cd/Pt	2ex	ac .515 ± 9
$CuSO_4$	0.168 m	0.2 g Ag		Cu/Pt	4ex	ac .356 ± 38

1903. A. Charpentier.

Sur le transport électrolytique de certains ions dans la gélatine. Comptes rendus, *136*, 1652.

The author finds that the chromate ion of chromic acid and potassium bichromate moves in gelatine toward the anode with velocity comparable to that of $H^{\cdot}$ or OH'; no reference is made to cataphoresis.

1903. R. B. Denison.

Beiträge zur direkten Messung von Ueberführungszahlen. Zeit. phys. Chem., *44*, 575.

For apparatus and method, see Steele, 1901; allowance for cataphoresis as in Abegg und Gaus, 1902. In some of the experiments with strontium chloride and lithium chloride the solutions contained gelatine, liquid or solid as indicated below. Electrodes Cu. A qualitative experiment showed the existence of complex anions in copper acetate solution.

NaCl	0.5m	LiCl, $NaC_2H_3O_2$	5ex	ac.618 ± 1	
NaBr	0.5m	" "	6ex	ac.619 ± 6	
KCl	0.5m	" "	3ex	ac.510 ± 2	
KBr	0.5m	" "	4ex	ac.505 ± 3	
K_2CrO_4	0.5m	" "	4ex	ac.484 ± 4	
$CaCl_2$	0.5m	$CdSO_4$, "	3ex	ac.666 ± 1	
$MgCl_2$	0.5m	" "	3ex	ac.685 ± 3	
	1.0	" "	3	ac.697 ± 0	
$MgSO_4$	0.5m	" "	3ex	ac.682 ± 2	
	1.0	" "	3	ac.698 ± 0	
	2.0	" "	3	ac.717 ± 3	
LiCl	0.5m	" "	3ex	ac.718 ± 2	
	1.0	" "	4	ac.734 ± 5	
	0.5	—, $Cu(C_2H_3O_2)_2$?	2	ac.738 ± 0	solid gelatine
	1.0	" "	2	ac.729 ± 4	" "
$SrCl_2$	0.5m	$CdCl_2$, $NaC_2H_3O_2$	2ex	ac.635 ± 0	
	1.0	$MgCl_2$, "	4	ac.641 ± 1	
	0.5	Cu, —	4	ac.652 ± 3	solid gelatine
	1.0	" "	2	ac.671 ± 1	" "
	0.5	Mg, —	3	ac.634 ± 1	gelatine liquefied
	1.0	" "	1	ac.648	" "

1903. Goldberger.

(Quoted by W. A. Roth Zeit. phys. Chem., *42*, 210, from unpublished experiments.)

$BaCl_2$. In the following table the volume percent of ethyl alcohol is given at the head of the column, the concentration of the barium chloride in the first column.

	0	*10*	*20*	*25*	*30*	*40*
0.033m	.543	.531	.540	.549	—	.533
0.017	.548	.536	.543	.551	.545	.536
0.011	.553	.545	.547	.550	—	.536
0.008	.554	.546	—	—	—	—

1903. Hornbostel.

(Quoted by W. A. Roth, Zeit. phys. Chem. *42*, 210, from unpublished experiments.)

KCl	0.034–0.0084m	18°	12ex	$-.494 \pm 4$ in 10 volume percent alcohol.
	0.034–0.011	18°	9	$-.481 \pm 5$ " 25 " " "

1903. R. Kremann.

Ueberführungsversuche zur Entscheidung der Konstitution von Salzen. Zeit. anorg. Chem., *33*, 87 (see also polemic, ibid., *35*, 48).

The formulæ of Werner for purpureo-cobalt-chloride $(ClCo(NH_3)_5).Cl_2$ was confirmed by the movement of the colored solution (rendered heavier by cane sugar) toward the cathode when electrolyzed in a U-tube between an anode solution of Na_2SO_4 and a cathode solution of H_2SO_4; for the praseobisulphate, by its similar behavior; and for diamine-cobalt-potassium-nitrite, by its movement toward the anode, between solutions of H_2SO_4 (anode) and acetic acid (cathode). The results were checked by direct electrolysis of the pure solution in a W-shaped tube and analysis of the solution in the neighborhood of the electrode; in the case of chlorpurpureo-cobalt-nitrate $(ClCo(NH_3)_5).(NO_3)_2$ the amount of chlorine in the neighborhood of the zinc cathode increased on electrolysis, and was lessened at the anode; in the case of the diamine-cobalt-potassium-nitrite the cobalt collected in the neighborhood of the anode.

Bredig's conception of methyl orange as an amphoteric electrolyte was discredited by the fact that when a strongly acid solution was electrolyzed in a U-tube between solutions of acid no movement of the colored layer toward the cathode could be detected; on the other hand, when the methyl orange solution was only weakly acid, or alkaline, the colored solution moved toward the anode.

The existence of "copper-, cobalt-, and nickel-phosphites" (*e. g.*, $Na.CuPO_3$) is deduced from the movement of the heavy metal toward the anode.

The movement toward the anode of the green solution of chromic hydroxide in strong alkali demonstrates the existence of chromites; the chromic hydroxide is not merely dissolved as colloid, for it can diffuse through parchment into alkaline solution. Similarly the zinc in potassium zincate becomes more concentrated at the anode.

1903. S. C. Lind.

The Constitution of Potassium Ruthenium Nitroso-chloride in Aqueous Solution. Jour. Am. Chem. Soc., *25*, 928.

A 0.025 m solution was connected by siphons containing 0.05 m potassium chloride solution solidified by agar agar with anode and cathode compartments containing Pt electrodes surrounded by hydrochloric acid and potassium hydrate respectively. A pink color moved toward the anode while no color change occurred in the cathode siphon. This shows that ruthenium is contained in an anion, presumably $RuCl_5NO''$; the author further concluded that it proved that no cation contains ruthenium.

1903. J. W. McBain.

Electrolytic Migration in Solutions of the Weak Acids.' This paper has not been published in full; abstracts have appeared in Trans. Roy. Soc. Canada, May, 1903, and 1904, and in Trans. Am. Electrochem. Soc., *4*, 184. (1903).

Apparatus: many forms, mostly pairs of U tubes; capacity 40–350 c.c.; Pt. electrodes; 0.04g Ag; diaphragms of cloth or bundles of small tubes; 2–5 middle portions, the real one unchanged within 0.00 to 0.05 c.c. of decinormal alkali.

The author eliminated the irregular and uncontrollable reactions occurring at the electrodes during the electrolysis of acetic and propionic acids, which would otherwise have discredited the results, by surrounding the electrodes with long columns of solutions of sodium sulphate, sulphuric acid, hydrochloric acid, etc. This made the apparatus complicated and the manipulation difficult. The electrode solutions were carefully tested for in the middle portions, but were usually altogether absent, and in no case present in quantity sufficient to cause an error of 20 percent in the result. An experiment with hydrochloric acid,

using the same apparatus and protecting solutions gave a normal result.

$H.C_2H_3O_2$	0.02–1.0m	30°	17ex	ac.31–
$H.C_2H_5O_2$	0.1m	30°	1	ac.34–
HCl	0.018m	30°	1	ac.19–

1903. P. Straneo.

Zeit. phys. Chem., *44*, 640, from Rendic. Accad. Lincei, 1902, *1*, 58, 171.

The author measured the E.M.F. between two electrodes placed in a solution of zinc sulphate just after a momentary current had been passed through; the migration value calculated from the concentration changes thus indicated agreed with that obtained by the usual analytical method.

1903. F. Vogel.

Untersuchungen über Nitrite. Zeit. anorg. Chem., 35, 410.

Apparatus like Jahn's; capacity of anode compartment 187 c.c.; Cd anode; middle portion unchanged. The barium was determined as $BaSO_4$. The results are calculated incorrectly (based on constant weight of solution instead of constant amount of water).

$Ba(NO_3)_2$	0.025–0.032m	0.3–0.6g Ag	2ex	a.588 ± 6

1904. F. Aletter.

Die Jonenkonzentrationen ternärer Elektrolyte. Dissert. Rostock, results quoted by Kümmel, Zeit. f. Elektrochem., *11*, 98, 1905.

Pt electrodes; no middle portion; capacity of cathode compartment 100 c.c.; method of calculation incorrect (based on constant volume of solution instead of on constant amount of solvent). Further I think the number given below as the migration of the C_2O_4'' ion is really that of the cation $K^{\cdot}$. In the case of lithium sulphate Aletter's calculation contains, in addition to the two systematic errors I have already mentioned, the further assumption that SO_4'' is monovalent. In the last column I have eliminated all but the first error.

				Aletter.	McBain.
$K_2C_2O_4$	1.0 m	16°	0.2 g Ag	c.24–	.76–
	0.5	16°	0.17	c.262	.738
Li_2SO_4	1.0 m	16°	0.27g Ag	a.652	.696
	0.5	16°	0.28	a.63–	.74–
	0.25	16°	0.17	a.60–	.80–

1904. J. S. Bridges.

The Transference Numbers of Copper Chloride in Concentrated Solution. Thesis presented for degree of B.Sc. Mass. Inst. of Tech., Boston.

Inaccessible in Heidelberg.

1904. C. H. Burgess and D. L. Chapman.

The Nature of a Solution of Iodine in Aqueous Potassium Iodide. Jour. Chem. Soc., *85*, 1305.

The authors deduce from the results of the comprehensive study of solutions of iodine in potassium iodide by previous investigators that KI and KI_3 are equally "strong" (*i. e.*, the dissociation constants are equal). Proceeding from this, and making use of the equilibrium constant for $I_2 + I' = I_3'$, they show that the relative rates of the I_3' and I' ions may be deduced from the migration value (that of KI being known) and independently by the measurement of the conductivity of potassium iodide solutions with and without the addition of iodine.

Apparatus: too complex for description without a figure; Pt electrodes; no middle portion; no diaphragms; 25°C.; the results are based (inaccurately) on constant volume of solution instead of constant weight of water. The KI was from 0.025 m to 0.5 m, the added I_2 0.0075–0.06 m.

The transport method gave as ratio of the mobilities of the I_3 and the I ions 0.556; the conductivity method 0.553.

1904. C. Dempwolff.

Jonenwanderung in Methylalkohol als Lösungsmittel. Zeit. f. Elektrochem., *11*, 124 (from Physik. Zeit., *5*, 637).

Apparatus shaped like an N with branch at right hand upper corner; no diaphragms; Ag, Cd, and Pt electrodes; 19°.

KI	0.336m	ac.49–	LiBr	0.719m	ac.69–	LiCl	0.840m	c.67–
	0.167	ac.44–		0.234	ac.65–		0.182	c.59–
	0.080	ac.37–		0.087	ac.56–		0.096	c.54–
	0.049	ac.33–		0.046	ac.55–		0.083	c.53–
	0.019	ac.32–					0.049	c.52–
$AgNO_3$	0.096m	ac.58–	KCl	0.039m	c.47–	KBr	0.092m	ac.45–
	0.049	ac.56–		0.021	c.44–		0.052	ac.43–
	0.033	ac.56–		0.017	c.44–		0.034	ac.42–
	0.024	ac.56–						
$NaCH_3O$	(Sodium methylate)		NaI	0.0803m	ac.55–			
	0.079m	ac.67–						
	0.037	ac.58–						
	0.026	ac.56–						

1904. E. C. Franklin and H. P. Cady.

On the Velocities of the Ions in Liquid Ammonia Solutions. Jour. Am. Chem. Soc., *26*, 499.

As the Journ. Am. Chem. Soc. is inaccessible in Heidelberg, I have abstracted this paper from Danneel's reviews (Beiblätter,

28, 971, and Zeit. f. Elektrochem., *11*, 109). Apparently two methods were used, both being meniscus-velocity methods. The simultaneous measurement of the velocities of the anion and cation succeeded only in the case of NH_4NO_3. The other measurements were made in a complex "sehr sinnig ausgedachtem" apparatus, and the migration values were deduced with the help of conductivity measurements. The indicators used were Hg-, Pb-, Cu- and Bi-salts at the anode, and picric acid at the cathode. The concentrations lay mostly between 0.5 and 0.01 m; temperature — 34°C. In NH_4Cl and NH_4Br the migration value increases rapidly with the concentration.

NH_4NO_3 .570 KNO_3 .501 $NaNO_3$ .574 NaCl .581 $AgNO_3$ .614

1904. H. C. Jones and H. P. Bassett.

Determination of the Relative Velocities of the Ions of Silver Nitrate in Mixtures of the Alcohols and Water, and on the Conductivity of such mixtures. Am. Chem. Jour., *32*, 409.

Apparatus: an M-tube with a glass tap in the middle dividing the whole into a cathode and an anode portion; capacity 130 c.c.; Ag electrodes; no diphragms; no middle portion; the results are incorrectly calculated (based on volume of solution, not amount of solvent). In the last column below is given the solvent; the authors do not mention whether the mixtures were made by weight or by volume.

$AgNO_3$					
0.1 m	25°	0.35g Ag	5ex	ac.529 ± 8	water
0.102	0°	0.12	3	ac.563 ± 0	"
0.08–0.1	25°	0.08	6	ac.598 ± 11	ethyl alcohol
0.10	25°	0.15	5	ac.580 ± 8	methyl alcohol
0.97	0°	0.06	5	ac.587 ± 6	" "
0.1	25°	0.12	3	ac.554 ± 3	25% methyl alcohol, 75% water
0.104	0°	0.08	8	ac.538 ± 10	25" " " 75" "
0.104	25°	0.11	3	ac.601 ± 5	50" " " 50" "
0.105	0°	0.6	3	ac.530 ± 1	50" " " 50" "
0.105	25°	0.08	5	ac.590 ± 3	75" " " 25" "
0.098	0°	0.06	6	ac.567 ± 2	75" " " 25" "

1904. V. Kohlschütter.

Ueber komplexe Kupferverbindungen. Ber., *37*, I, 1153.

Apparatus: four U-tubes connected by siphons; capacity 12 c.c.; no middle portions. On account of the extraordinary influence of the concentration on the migration value I have given in the second column below directly the weight of $CuCl_2$

in 1000 g. H_2O. In qualitative experiments it was found that the yellow color of a concentrated solution of cupric chloride in hydrochloric acid moved toward the anode into a concentrated solution of hydrochloric acid or magnesium calcium or lithium chloride, proving the presence of complex anions. When concentrated cupric chloride solution was electrolysed between layers of ammonium or sodium sulphate or acetate, the boundary on the anode side remained stationary, while a blue color moved towards the cathode. The method of calculation is correct. I think that the probable explanation of the extraordinary influence of the concentration on the migration value is to be sought for in the excessive hydration of the cation. Surely the fourth experiment must be a mistake.

$CuCl_2$	711.3g = 5.29 mols		0.67g Ag	1ex	c 1.835
	584.4g = 4.35 "		0.37	1	c 1.632
	500.9g = 3.72 "		0.37	1	c 1.411
	445.4g = 3.3 "		0.53	1	c—0.795
	357.5g = 2.66 "	— 1.35°	0.39	1	c .817
	357.5g = 2.66 "	+ 17.95°	0.47	1	c 1.042

1904. T. W. Richards and F. Bonnet.

Das veränderliche hydrolytische Gleichgewicht von gelöstem Chromsulphat. Zeit. phys. Chem., *47*, 46. Proc. Am. Acad. Arts and Sci., June, 1903.

Apparatus: four glasses superposed upon a U-tube; Cd electrodes; parchment diaphragms.

A solution of green chromium sulphate saturated with chromic hydroxide was placed in the middle vessel while the four other vessels were filled with a solution of cadmium sulphate. No chromium was moved towards the anode; $n = .26$ — if the cation containing chromium is divalent, $n = .63$ — if monovalent. The possibility of the presence of a colloid is not discussed.

1904. O. F. Tower.

Transport number of Sulphuric Acid. Jour. Am. Chem. Soc., *26*, 1038. Jour. de chim. physique, *3*, 1. [Abs. W.L.M.]

Apparatus: two U-tubes with side apertures connected by rubber tubing, 40 cm. long and 3 cm. diameter; in a smaller apparatus (S.A.) the diameter was 2 cm. Anode, Cd; cathode, Pt spiral. Average current 0.07 amp, in a few cases twice as much. Duration of electrolysis, 2–3 hours. After electrolysis the solution was analyzed in 5 portions; in every case the composition of the middle portion remained constant within the error

of analysis, *i. e.*, 0.0009g of H_2SO_4 for normal and half normal acid, and 0.0005g for more dilute solutions.

H_2SO_4	normal	20°	0.74g Ag	3ex	ac.188 ± 6 (S.A.)
	"	20	0.6–1.4	6	ac.188 ± 9
	0.5n	20	0.7–1.3	6	ac.187 ± 6
	0.2	20	0.8	6	ac.180 ± 7 (S.A.)
	0.1	8	0.7	6	ac.164 ± 4
	0.1	20	0.7	6	ac.174 ± 6 (S.A.)
	0.1	20	0.7	6	ac.176 ± 1
	0.1	32	0.6	6	ac.192 ± 1
	0.05	8	0.4	6	ac.164 ± 2
	0.05	20	0.3	4	ac.176 ± 4 (S.A.)
	0.05	20	0.3–0.6	6	ac.179 ± 3
	0.05	32	0.5	6	ac.192 ± 2
	0.02	8	0.2	6	ac.168 ± 2
	0.02	20	0.25	6	ac.181 ± 3
	0.02	32	0.25	6	ac.191 ± 3

The author considers the following to be the most trustworthy results; but thinks that .1764 for $n/10$ acid at 20° is "for some unaccountable reason" too low.

Concentration.	Temp. 8°	20°	32°
Normal	—	.1877	—
0.5n	—	.1869	—
0.2	—	.1805	—
0.1	.1644	.1764	.1917
0.05	.1637	.1791	.1916
0.02	.1681	.1809	.1912

The author summarized his results with dilute solutions in the formula:

$$n_t = 0.1788 + 0.0011(t - 20)$$

1905. **R. Luther und B. Krsnjavi.**

Ueber komplexe Verbindungen der Kohlensäure mit Schwermetallen. Zeit. anorg. Chem., *46*, 170.

Solutions of cupric (sulphate), ferric, or uranyl salts in excess of alkali bicarbonate solution were placed in the bottom of a U-tube, both branches of which were filled with potassium bicarbonate solution; on passing through an electric current the colored zone moved toward the anode (slowly, at least in the case of the cupric compound). Taken in conjunction with the observation that these bodies diffuse through parchment, this shows the presence of the metals in the complex anions.

1905. C. Tubandt.

Ueber die alkalischen Kobaltoxydullösungen. Zeit. anorg. Chem., *45*, 368.

The blue solution obtained by dissolving cobaltous hydroxide in concentrated potash or by the electrolysis of strong potash with a cobalt anode contains the cobalt (or hydroxide) only as colloid, for it does not dialyse through parchment into concentrated potash; when a current of 0.1 ampere was passed through the solution placed in the lower half of a U-tube both arms being filled with potash solution the blue layer did not move perceptibly in several hours; in 36 hours all the cobalt was precipitated, mostly as metal on the cathode, some as oxide in the anode compartment, none on the anode. Addition of glycerine has no influence on any of these phenomena.

1906. H. Jahn's Pupils.

For the following series I am indebted to the courtesy of Professor Jahn, who voluntarily sent me his own copies of the dissertations, as they are out of print. He expects to publish them together in the Zeit. phys. Chem. in the course of the present winter.

Apparatus and method the same as in the 1901 series; capacity of anode compartment 300–800 c.c.; anode Cd or Zn, cathode Hg covered with a concentrated solution of $CdSO_4$ or sometimes $ZnCl_2$.

E. Berliner.

Dissert., 1902.

Ag anode, cathode Hg covered with $Cu(NO_3)_2$.

The paper further contains measurements of the transport in mixtures of $AgNO_3$ and KNO_3 showing that the mobility of the Ag ion is not appreciably affected by the presence of the potassium nitrate.

$AgNO_3$	0.498m	18°	0.8g Ag	0.00–0.09 %	3ex	a.516 ± 5
	0.249	18°	0.5	0.02–0.1	3	a.519 ± 5
	0.124	18°	0.5	0.00–0.1	3	a.526 ± 1
	0.068–0.0166	18°	0.4	0.02–0.5	7	a.528 ± 3
	0.0111–0.0047	18°	0.1–0.4	0.00–0.1	7	a.531 ± 5
	0.5–0.007	30°	0.3–0.7	0.01–0.2	27	a.519 ± 7

A. Eisenstein.

Dissert., 1902, quoted by Roth, Zeit. phys. Chem., *42*, 210. 1903.

The middle layer of solution never showed the least trace of

zinc — from anode or cathode; the change in composition is therefore ascribed to evaporation of the ethyl alcohol.

NaCl

0.034m	18°	0.3g Ag	0.07–0.15 %	3ex	a.599 ± 2	10 vol. % alcohol
0.017–0.009	18	0.2–0.3	0.05–0.3	9	a.594 ± 3	10 " " "
0.033	18	0.6	0.3 –0.4	3	a.592 ± 0	20 " " "
0.017–0.011	18	0.25	0.1 –0.4	7	a.588 ± 2	20 " " "
0.0084	18	0.23	0.1 –0.3	3	a.586 ± 1	20 " " "
0.033–0.011	18	0.2–0.5	0.0 –0.3	9	a.584 ± 3	25 " " "
0.033–0.011	18	0.2–0.7	0.1 –0.4	11	a.578 ± 5	30 " " "
0.033	18	0.3	0.1 –0.15	2	a.578 ± 2	40 " " "
0.017	18	0.23	0.1 –0.3	4	a.575 ± 3	40 " " "
0.011	18	0.2	0.3 –0.4	3	a.573 ± 1	40 " " "

S. Goldlust.
Dissert., 1902.

K_2SO_4	0.0333m	18°	0.6g Ag	0.02–0.04 %	3ex	a.512 ± 1
	0.0167	18	0.4	0.01–0.05	4	a.510 ± 2
	0.0089–0.004	18	0.13–0.35	0.03–0.15	9	a.516 ± 2
Na_2SO_4	0.0332m	18°	0.3–0.6g Ag	0.01–0.12 %	4ex	a.621 ± 2
	0.0167	18	0.4	0.13–0.16	3	a.613 ± 1
	0.008–0.004	18	0.3	0.01–0.2	9	a.609 ± 2
$CdSO_4$	0.0333m	18°	0.3–0.4g Ag	0.01–0.04 %	3ex	a.631 ± 2
	0.0167	18	0.4	0.09	3	a.619 ± 2
	0.0084–0.0042	18	0.23–0.37	0.02–0.12	9	a.613 ± 1

A. Hertz.
Dissert., 1904.

KCl	0.2–0.05m	18°	0.4 –0.7g Ag	0.2 –0.03 %	9ex	a.506 ± 4
	0.2–0.03	30°	0.14–0.8	0.05	12	a.502 ± 3
	0.02–0.007	30°	0.1	0.1 –0.01	12	a.501 ± 1
	0.2–0.03	0°	0.14–0.6	0.1 –0.00	12	a.509 ± 2
	0.017	0°	0.15	0.03	3	a.507 ± 2
	0.011–0.0086	0°	0.1	0.07–0.01	6	a.506 ± 2
	0.0067	0°	0.1	0.1 –0.01	3	a.505 ± 0
NH_4Cl	0.034m	0°	0.13g Ag	0.04–0.01	3ex	a.513 ± 1
	0.017	0°	0.12	0.04–0.00	3	a.511 ± 2
	0.011–0.0084	0°	0.12	0.1 –0.00	6	a.510 ± 1

M. Huybrechts.
Dissert., 1902.

$MgSO_4$	0.0339m	18°	0.3 –0.5g Ag	0.01–0.02 %	3ex	a.631 ± 1
	0.0172	18°	0.3	0.00–0.04	3	a.624 ± 2
	0.0085	18°	0.26	0.01–0.10	3	a.619 ± 1
	0.006–0.0034	18°	0.22	0.03–0.09	9	a.614 ± 2
	0.0339	30°	0.3 –0.8	0.01–0.03	3	a.624 ± 2
	0.0168	30°	0.4	0.01	3	a.616 ± 2
	0.0083–0.006	30°	0.3	0.00–0.05	6	a.613 ± 1

H_2SO_4	0.124m	18°	1.1g Ag	0.02–0.05	3ex	a.168 ± 3
	0.062–0.0055	18°	0.3 –0.9	0.00–0.06	14	a.176 ± 4
	0.0052	18°	0.17	0.00–0.02	3	a.173 ± 1
	0.00465	18°	0.12	0.00–0.06	3	a.157 ± 3
	0.00499	18°	0.12	0.00–0.10	3	a.155 ± 4
	0.0309	30°	0.4 –0.6	0.01–0.05	3	a.195 ± 4
	0.0176	30°	0.4 –0.5	0.01–0.03	3	a.188 ± 1
	0.0085	30°	0.3 –0.5	0.00–0.07	3	a.186 ± 2
	0.00600	30°	0.25	0.02–0.04	3	a.184 ± 0
	0.00484	30°	0.12	0.04–0.09	3	a.170 ± 2
	0.00464	30°	0.13	0.12	1	a.161
	0.00404	30°	0.17	0.02–0.05	3	a.162 ± 3

Joachim.

Dissert., as yet unpublished.

HCl	0.0321m	18°	a.165
	0.0166	18°	a.167
	0.0112	18°	a.166
	0.0083	18°	a.167
	0.0066	18°	a.168

H. Schultz.

Dissert., 1904.

I think that the author would have been justified in calculating his results to the fourth decimal place.

NaCl	0.118m	0°	0.3–0.5g Ag	0.00–0.07%	3ex	a.615 ± 1
	0.073	0°	0.3	0.00–0.04	3	a.614 ± 1
	0.034–0.012	0°	0.13–0.2	0.00–0.04	9	a.613 ± 1
	0.0085–0.0067	0°	0.1	0.01–0.03	6	a.612 ± 0
	0.118–0.072	18°	0.3–0.5	0.00–0.03	6	a.605 ± 1
	0.119–0.031	30°	0.1–0.45	0.00–0.03	9	a.597 ± 1
	0.016–0.010	30°	0.11–0.19	0.00–0.02	6	a.596 ± 1
	0.0086–0.0067	30°	0.11	0.00–0.03	6	a.595 ± 0
NH_4Cl	0.034m	18°	0.24g Ag	0.01–0.06	3ex	a.510 ± 0.5
	0.017	18°	0.22	0.00–0.01	3	a.509 ± 0.5
	0.012	18°	0.16	0.00–0.02	3	a.508 ± 0.5
	0.0083	18°	0.15	0.02–0.06	3	a.507 ± 0.5
	0.034	30°	0.2–0.3	0.00–0.05	3	a.506 ± 0.5
	0.017	30°	0.14–0.2	0.00–0.02	3	a.505 ± 0.0
	0.012	30°	0.13	0.00–0.04	3	a.505 ± 0.5
	0.0083	30°	0.1–0.14	0.00–0.01	3	a.504 ± 0.0

E. Wolff.

Dissert., 1903.

HCl	0.1202m	0°	0.6–1.2g Ag	0.01–0.14%	3ex	a.167 ± 2
	0.0640	0°	0.5–0.7	0.02	3	a.161 ± 2
	0.0318	0°	0.4–0.6	0.02	3	a.160 ± 1
	0.0160	0°	0.2	0.02–0.04	3	a.155 ± 1
	0.0106–0.0064	0°	0.2	0.01–0.2	9	a.154 ± 3
	0.12–0.006	30°	0.2–1.0	0.00–0.2	21	a.183 ± 4

$BaCl_2$	0.0165m	0°	0.22g Ag	0.02–0.18	3ex	a.573 ± 2
	0.0084	0°	0.16	0.03–0.05	3	a.566 ± 1
	0.0056–0.0034	0°	0.08–0.15	0.00–0.2	9	a.562 ± 2
	0.016–0.008	30°	0.24–0.4	0.02–0.12	6	a.557 ± 2
	0.005–0.003	30°	0.2	0.00–0.2	9	a.555 ± 2

INDEX OF CHEMICALS.

In the following alphabetical list, each substance is given under the symbol of its cation or metal and is followed by the names of the experimenters who have worked with it, together with the dates of the papers; this facilitates reference to the chronological compilation of the data. In addition, anions are given; these are followed by a list of the cations of the combinations which have been experimented with. Thus after "SO_4" are found the metals whose sulphates have been studied, and to which the reader is referred for the names of the experimenters. The papers in brackets are those in which the chemicals used were merely incidental, or in which the experiments were only qualitative.

$AgBr+Hg(NO_3)_2$ (Morse, 1902)

$AgC_2H_3O_2$ Hittorf, 1853; Loeb and Nernst, 1888; Mather, 1897; Bein, 1898; Hoffmeister, 1898

$Ag(C_2H_5)SO_4$ Loeb and Nernst, 1888

$Ag(C_6H_5)SO_3$ Loeb and Nernst, 1888

$Ag(C_9H_{11})SO_3$ Loeb and Nernst, 1888

$Ag(C_{10}H_7)SO_3$ Loeb and Nernst, 1888

AgCN.KCN Hittorf, 1859 (Noyes and Blanchard, 1901)

$AgCl+Hg(NO_3)_2$ (Morse, 1902)

$AgClO_3$ Loeb and Nernst, 1888; Carrara, 1903

$AgClO_4$ Loeb and Nernst, 1888

$Ag_3Cr(C_2O_4)_3$ Kistiakowsky, 1890, 1901

$AgI+KI$ Rieger, 1901

$AgI+Hg(NO_3)_2$ (Morse, 1902)

$Ag_3I(NO_3)_2$ (Hellwig, 1900)

$AgNO_3$ Hittorf, 1853; Wiedemann, 1856; (Lodge, 1886); Nernst and Loeb, 1888; Kistiakowski, 1890; (Chassy, 1890); Bein, 1892; Campetti, 1894; (Whetham, 1895); Mather, 1897; Bein, 1898; Hoffmeister, 1898; Berliner, 1901; Steele, 1902; Schlundt, 1902; Carrara, 1903; Jones and Bassett, 1904; Dempwolff, 1904; Franklin and Cady, 1904; Berliner, 1906

$Ag_2S_2O_6$ Loeb and Nernst, 1888

Ag_2SO_4 Hittorf, 1853; (Chassy, 1890)

Ag_2SiFl_6 Loeb and Nernst, 1888

$AlCl_3$ Hittorf, 1859

$Al_2O_3.K_2O.4C_2O_3.7\frac{1}{2}H_2O$ Rosenheim, 1896

$Al_2O_3.3K_2O.6C_2O_3.5H_2O$ Rosenheim, 1896

$Al_2(SO_4)_3.K_2SO_4.24H_2O$ (Daniell and Miller, 1844)

$Al_2(SO_4)_3$ (Daniell and Miller, 1844)

AsO_3...K

AsO_4...K

$AuCl_3.KCl$ Hittorf, 1859

$AuCl_3O.H_2$ Hittorf and Salkowski, 1899 (Pouillet, 1845)

$BaCl_2$ Weiske, 1857; Hittorf, 1859; (Lodge, 1886); (Chassy, 1890); Bein, 1892; (Whetham, 1895); Des Coudres, 1896; Hopfgartner, 1898; Bein, 1898; Noyes, 1901; Bukschnewski, 1901; Steele, 1902; Hittorf, 1902; Wolff, 1906

$Ba(NO_2)_2$ Vogel, 1903
$Ba(NO_3)_2$ Daniell and Miller, 1844; (Chassy, 1890); Noyes, 1901; Hittorf, 1859
$Ba(OH_2)$ Daniell, 1840
BrO_3...K
Br...Na-Cd-H-K-Zn-AgHg-Li
CH_3ONa Dempwolff, 1904
$C_2H_3O_2$...H-Ag-Cd-Cu-Fe-Li-Na-K-UO_2-Zn
$C_2H_5.SO_4$...Ag-K
$C_3H_5O_2$ (propionate)...H-UO_2
$C_4H_4O_4$ (succinate)...H
$C_4H_4O_6$ (tartrate)...KNa-(Fehling's solution)-UO_2
$C_6H_5.OH.NO_2$ (ortho-nitro-phenol) (Riesenfeld, 1901)
$C_6H_5.SO_3$...Ag
$C_9H_{11}.SO_3$...Ag
$C_{10}H_7.SO_3$...Ag
$C_{17}H_{19}NO_3.HCl$ (morphine) Hittorf, 1859
$C_{22}H_{22}N_2O_2.HCl$ (strychnine) Hittorf, 1859
CN...Ag.K-Cd-Hg-K-Zn-K.Cd-KFe-HFe-KHg-KZn
CNS...K-Fe
C_2O_4...H-Ag-Cr.Ag_2-K.Fe-K-NH_4
$C_2O_3.K_2O.WO_3.H_2O$ Rosenheim, 1896
$4C_2O_3.K_2O.Al_2O_3.7\frac{1}{2}H_2O$ Rosenheim, 1896
$2C_2O_3.2MO_3.3H_2O.(NH_4)_2O$ Rosenheim, 1896
$2C_2O_3.(NH_4)_2O.2MO_3.3H_2O$ Rosenheim, 1896
$4C_2O_3.3(NH_4)_2O.V_2O_5.4H_2O$ Rosenheim, 1896
$6C_2O_3.5H_2O.3K_2O.Al_2O_3$ Rosenheim, 1896
$6C_2O_3.3K_2O.Cr_2O_3.6H_2O$ Rosenheim, 1896
$C_2O_3.MO_3.3H_2O$ Rosenheim, 1896
CO_3...K-Li-Na-Cu-Fe-UO_2
$CaCl_2$ Weiske, 1857; Hittorf, 1859; (Chassy, 1890); (Whetham, 1892); Bein, 1892; (Whetham, 1895); Bein, 1898; Bein, 1899; Steele and Denison, 1902; Steele, 1902; Hittorf, 1902; Denison, 1903
CaI_2 Hittorf, 1859
$Ca(NO_3)_2$ Hittorf, 1859; (Whetham, 1892); Steele and Denison, 1902
$Ca(OH)_2$ Bein, 1898
$CaSO_4$ Daniell and Miller, 1844; Steele and Denison, 1902
$CdBr_2$ Gordon, 1897; Kümmell, 1898; Goldhaber, 1901; Bukschnewski, 1901
$Cd(C_2H_3O_2)_2$ Carrara, 1903
$Cd(ClO_3)_2$ Carrara, 1903
$CdCl_2$ Hittorf, 1859; Bein, 1892; Des Coudres, 1896; Bein, 1898; Kümmell, 1898; Bein, 1899; Goldhaber, 1901; Bukschnewski, 1901; Hittorf, 1902; Carrara, 1903
$Cd(CN)_2 + KCN$ Rieger, 1901
CdI_2 Hittorf, 1859; Lenz, 1882; Bein, 1892; Gordon, 1897; Kümmell, 1898; Redlich, 1901; Bukschnewski, 1901; Hittorf, 1902; Carrara, 1903
$CdI_2 + KI$ Hittorf, 1859
$Cd(NO_3)_2$ Carrara, 1903
$CdSO_4$ Weber, 1889; (Chassy, 1890); Gordon, 1897; Kümmell, 1898; Steele, 1901; Redlich, 1901; Goldlust, 1906
Cl Ag.Hg-Al-Au-Ba-$C_{17}H_{19}NO_3$.H-$C_{22}H_{22}N_2O_2$. H-Ca-Cd-Co-Co. Ca-Co. Ca. Zn-Co. H-Co. Hg-Co. Mg-Co. NH_2-Cs-Cu-CuH-Fe-Fe. H-H-H. Pt-K-K. Au-K. Cd-K. Hg-Li-Mg-Mn-Na-Na. Pt-NH_4-Pt-Rb-RuK_2 NO-Sn-Sr-Tl-UO_2-Zn
ClO_3...Ag-Cd-Cu-K-Li
ClO_4...Ag-K
Co (purpureocobaltchloride, praseo bisulphate, diamine-cobalt-potassium nitrite, chlor-purpureo-cobalt nitrate) (Kremann, 1903)
$CoCl_2 + HCl$ (Donnan and Bassett, 1902)
$CoCl_2 + MgCl_2$ (Donnan and Bassett, 1902)
$CoCl_2 + CaCl_2$ (Donnan and Bassett, 1902)
$CoCl_2 + CaCl_2 + ZnCl_2$ (Donnan and Bassett, 1902)
$CoCl_2 + HgCl_2$ (Donnan and Bassett, 1902)

$Co(CN)_6$...K
$Co(OH)_2$ + KOH (Tubandt, 1905)
$CoPO_3$...Na
$CoCl_2$ Pouillet, 1845; (Whetham, 1892); Bein, 1898; (Donnan and Bassett, 1902)
$Co(NO_3)_2$ (Chassy, 1890); (Whetham, 1892)
$CrAg_3(C_2O_4)_3$ Kistiakowsky, 1890, 1901
$Cr_2O_3.3K_2O.6C_2O_3.6H_2O$ Rosenheim, 1896
CrO_2...K
CrO_4...K-Cu-H
Cr_2O_7...K-H
$Cr_2(SO_4)_3$ Bonnet and Richards, 1904
CsCl Bein, 1898
$Cu(C_2H_3O_2)_2$ Carrara, 1903
$CuCl_2$ (Chassy, 1890); (Whetham, 1892); (Lussana, 1894); Bein, 1898; (Masson, 1898); (Noyes and Blanchard, 1901); Carrara, 1903; Bridges, 1904; Kohlschütter, 1904
$CuCl_2$ + HCl (Donnan and Bassett, 1902)
$Cu(ClO_3)_2$ Carrara, 1903
$CuCO_3$ (Luther and Krsnjavi, 1905)
$CuCrO_4$ (Noyes and Blanchard, 1901)
$Cu(NO_3)_2$ Wiedemann, 1856; (Chassy, 1890); Carrara, 1903
$CuPO_3$...Na
$CuSO_4$ (Daniell and Miller, 1844); Hittorf, 1853, 1856; Wiedemann, 1856; Kirmis, 1878; Lenz, 1882; (Lodge, 1886); Weber, 1889; (Chassy, 1890); Bein, 1892; Lussana, 1893; Sheldon and Downing, 1893; (Lussana, 1894); Gordon, 1897; (Küster, 1897); Schrader, 1897; Bein, 1898; Hopfgartner, 1898; Masson, 1898; (Masson and Setele, 1899); Metelka, 1901; Rieger, 1901; (Steele, 1901); Hittorf, 1902; Steele, 1902; Carrara, 1903
$CuSO_4.K_2SO_4$ (Daniell and Miller, 1844); Rieger, 1901
$CuSO_4$ + NH_4OH (Donnan and Bassett, 1902
Di-methyl-pyrone (Coehn, 1902)
$Fe(C_2H_3O_2)_2$ (Whetham, 1894)
$Fe(CNS)_3$ (Riesenfeld, 1901)
$Fe(CN)_6$...H-K
$FeC_2O_4.K_2C_2O_4$ Rieger, 1901
$Fe(C_2O_4)_3$...K
$Fe_2(CO_3)_2$ (Luther und Krsnjavi, 1905)
$FeCl_2$ (Pouillet, 1845); Hittorf, 1859; (Whetham, 1894)
$FeCl_2$ + HCl (Donnan and Bassett, 1902)
$FeFl_2.3NaFl$ (Peters, 1898)
Fehling's solution (Küster, 1897); (Masson and Steele, 1899); (Donnan and Bassett, 1902)
$FeSO_4$ (Lussana, 1894)
$Fe_2(SO_4)_3$ (Daniell and Miller, 1844); Peters, 1898
Fl...FeNa
H_2AuCl_3O Hittorf and Salkowski, 1899
HBr Hittorf, 1859; McIntosh, 1898
$H.C_2H_3O_2$ (Lodge, 1886); Schrader, 1897; Hoffmeister, 1898; McBain, 1903
$H.C_3H_5O_2$ McBain, 1903
$H_2.C_2O_4$ (Oxalic acid); (Bourgoin, 1870); Bein, 1898; McIntosh, 1898
$H_2.C_4H_4O_4$ (Succinic acid); Bourgoin, 1868; Bein, 1898
HCl Hittorf, 1859; (Lodge, 1886); Cattaneo, 1896; Des Coudres, 1896; Hopfgartner, 1898; McIntosh, 1898; Bein, 1898, 1899; Bogdan, 1901; Noyes and Sammet, 1902; Joachim, 1906; Wolff, 1906
H_2CrO_4 (Charpentier, 1903)
$H_4Fe(CN)_6$ (Porrett, 1814)
$HgBr_2$ + $Hg(NO_3)_2$ (Morse, 1902)
$HgCl_2$ + KCl Hittorf, 1859
$HgCl_2$ + $Hg(NO_3)_2$ (Morse, 1902)
$Hg(CN)_2.2KCN$ Rieger, 1901
HgI_2 + KI Rieger, 1901
HgI_2 + $Hg(NO_3)_2$ (Morse, 1902)
$Hg(NO_3)_2$ + AgCl, $HgCl_2$, AgBr, $HgBr_2$, AgI, or HgI_2 (Morse, 1902)
HI Hittorf, 1859; McIntosh, 1898
HIO_3 Hittorf, 1859
NOH_3 Wiedeman, 1856; Bourgoin, 1868; Bein, 1898; Hoffmeister, 1898; Bukschnewski, 1901
H_2O_2 + NaOH (Calvert, 1901)

$H_2.PtCl_4O$ Hittorf and Salkowski, 1899; Dittenberger and Dietz, 1899
H_2PtCl_6 Dittenberger and Dietz, 1899
H_3PO_4 Daniell, 1840
H_2SO_4 Faraday, 1833; Daniell, 1839, 1840; Wiedemann, 1856; Hittorf, 1859; Bourgoin, 1868; (Lodge, 1886); Schrader, 1897; McIntosh, 1898; Bein, 1898; Stark, 1899; Kendrick, 1900; Tower, 1904; Huybrechts, 1906
I...Ag-Ag.Hg-Ca-Cd-H-K-K.Cd-K.Hg-Li-Mg-Na-$N(C_2H_5)_4$-$S(CH_3)_3$-Zn
I_3...K
IO_3...H
K_3AsO_3 (Daniell and Miller, 1844)
K_3AsO_4 (Daniell and Miller, 1844)
KBr Hittorf, 1856; (Lodge, 1886); Bogdan, 1901; Steele, 1901, 1902; Riesenfeld, 1902; Denison, 1903; Dempwolff, 1904
$KBrO_3$ Steele, 1902
$KC_2H_3O_2$ Hittorf, 1856; Hittorf, 1856, 1858
$K(C_2H_5)SO_4$ Hittorf, 1859
KCN (Daniell and Miller, 1844); Hittorf, 1859; Rieger, 1901
KCN.AgCN Hittorf, 1859; (Noyes and Blanchard, 1901)
$KCN + Hg(CN)_2$ Rieger, 1901
$KCN + Zn(CN)_2$ Rieger, 1901
KCNS (Daniell and Miller, 1844)
K_2CO_3 Kuschel, 1881; (Whetham, 1892); (Whetham, 1894); Bein, 1898
$K_2C_2O_4$ Hittorf, 1859; (Whetham, 1892); Aletter, 1904
$K_2C_2O_4.FeC_2O_4$ Rieger, 1901
KCl Hittorf, 1856; Weiske, 1857; Hittorf, 1858; Kuschel, 1881; (Chassy, 1890); Bein, 1892; (Whetham, 1892); (Lussana, 1894); Des Coudres, 1896; Schrader, 1897; Bein, 1898; Masson, 1898; Hopfgartner, 1898; Bogdan, 1901; Steele, 1901; Abegg and Gaus, 1902; Hittorf, 1902; Riesenfeld, 1902; Steele, 1902; Steele and Denison, 1902; Denison, 1903; Dempwolff, 1904; Hertz, 1906
$KCl.AuCl_3$ Hittorf, 1859
$KCl.HgCl_2$ Hittorf, 1859
$KCl.2HgCl_2$ Hittorf, 1859
$KCl.4HgCl_2$ Hittorf, 1859
$KClO_3$ Hittorf, 1859
$KClO_4$ Hittorf, 1859
$K_3Co(CN)_6$ Kistiakowsky, 1901
KCo (diamine-nitrite) (Kremann, 1903)
$K_2Cr_2O_7$ Hittorf, 1859; (Whetham, 1892, 1894); Riesenfeld, 1901; (Charpentier, 1903)
K_2CrO_4 (Daniell and Miller, 1844; Hittorf, 1859; Lenz, 1882; Masson, 1898; (Steele, 1901); Steele, 1902; Denison, 1903
$K.CrO_2$ (Kremann, 1903)
$K_3Fe(CN)_6$ (Daniell and Miller, 1844)
$K_4Fe(CN)_6$ (Porrett, 1814); (Daniell and Miller, 1844); Hittorf, 1859; (Lodge, 1886); Kistiakowsky, 1901
$K_3Fe(C_2O_4)_3$ Rieger, 1901; Steele, 1902
KH_2PO_4 Hittorf, 1859
KI Hittorf, 1856, 1858; Lenz, 1882; (Lodge, 1886); Schrader, 1897; Bein, 1898; Rieger, 1901; Nernst and Riesenfeld, 1901; Riesenfeld, 1902; Dempwolff, 1904
KI_3 (Steele, 1902); Burgess and Chapman, 1904
$KI + HgI_2$ Rieger, 1901
$KI.CdI_2$ Hittorf, 1859
$KMnO_4$ (Whetham, 1892); Nernst, 1897; Bein, 1898
$KNa.C_4H_4O_4$ (Küster, 1897)
KNO_3 Hittorf, 1856, 1858; (Chassy, 1890); (Nernst, 1897); Franklin and Cady, 1904
$KNO_3 + AgNO_3$ Berliner, 1906
$3K_2O.Al_2O_3.6C_2O_3.5H_2O$ Rosenheim, 1896
$K_2O.Al_2O_3.4C_2O_3.7\frac{1}{2}H_2O$ Rosenheim, 1896
$3K_2O.Cr_2O_3.6C_2O_3.6H_2O$ Rosenheim, 1896
KOH Daniell, 1840; Wiedemann, 1856; Bourgoin, 1868; Kuschel, 1881; (Noyes and Blanchard, 1901); Steele, 1902
$KOH + Co(OH)_2$ (Tubandt, 1905)
$K_2O.WO_3.C_2O_3.H_2O$ Rosenheim, 1896

$K_2RuNOCl_5$ (Lind, 1903)
K_2SO_4 Daniell, 1840; (Daniell and Miller, 1844); Hittorf, 1856; (Chassy, 1890), Masson, 1898; Noyes, 1901; Goldlust, 1906
$K_2SO_4.Al_2(SO_4)_3 + 24H_2O$ (Daniell and Miller, 1844)
$K_2SO_4.CuSO_4$ (Daniell and Miller, 1844); Rieger, 1901
$K_2SO_4.MgSO_4$ (Daniell and Miller, 1844)
K_2ZnO_2 (Kremann, 1903)
LiBr Dempwolff, 1904
$Li.C_2H_3O_2$ Carrara, 1903
LiCl Kuschel, 1881; Campetti, 1894; Des Coudres, 1896; Bein, 1898; Masson, 1898; Bein, 1899; Goldhaber, 1901; (Steele, 1901); Steele, 1902; Riesenfeld, 1902; Denison, 1903; Dempwolff, 1904
$LiClO_3$ Carrara, 1903
Li_2CO_3 Kuschel, 1881
LiI Kuschel, 1881; Carrara, 1903
$LiNO_3$ Carrara, 1903
LiOH Kuschel, 1881
Li_2SO_4 Kuschel, 1881; Masson, 1898; Aletter, 1904
Methyl orange (Kremann, 1903)
$MgCl_2$ Hittorf, 1859; Bein,. 1898; (Chassy, 1890); Steele, 1902
MgI_2 Hittorf, 1859
$Mg(NO_3)_2$ (Chassy, 1890)
$MgSO_4$ Hittorf, 1859; (Chassy, 1890); Bein, 1898; Hopfgartner, 1898; Masson, 1898; Steele, 1901, 1902; Denison, 1903; Huybrechts, 1906
$MgSO_4.K_2SO_4$ (Daniell and Miller, 1844)
$MnCl_2$ Pouillet, 1845; Hittorf, 1859; Bein, 1898
$MnO_4...K$
$MO_3.C_2O_3.3H_2O$ Rosenheim, 1896
$2MO_3.2C_2O_3.(NH_4)_2O.3H_2O$ Rosenheim, 1896
$2MO_3.C_2O_3.(NH_4)_2O$ Rosenheim, 1896
$2MO_3.(NH_4)_2O$ Rosenheim, 1896
Morphine hydrochloride Hittorf, 1859
NaBr Bein, 1898; Bogdan, 1901; Oppenheimer, 1901; Steele, 1901, 1902; Denison, 1903
$NaCH_3O$ Dempwolff, 1904
$NaC_2H_3O_2$ Hittorf, 1859; (Chassy, 1890); (Whetham, 1894); (Steele, 1901); Abegg and Gaus, 1902
NaCl (Daniell and Miller, 1844); Wiedemann, 1856; Weiske, 1857; Hittorf, 1859; (Lodge, 1886); (Chassy, 1890); Bein, 1892; (Lussana, 1894); (Whetham, 1895); Cattaneo, 1896; Des Coudres, 1896; Bein, 1898; Hopfgartner, 1898; Masson, 1898; Bein, 1899; Bogdan, 1901; Steele, 1901, 1902; Abegg and Gaus, 1902; Denison, 1903; Franklin and Cady, 1904; Eisenstein, 1906; Schulz, 1906
Na_2CO_3 (Daniell and Miller, 1844); Kuschel, 1881; (Whetham, 1895); Bein, 1898
$Na.CoPO_3$ (Kremann, 1903)
$Na.CuPO_3$ (Kremann, 1903)
$3NaFl + FeFl_3$ (Peters, 1898)
Na_2HPO_4 Hittorf, 1859
NaH_2PO_4 (Daniell and Miller, 1844); Hittorf, 1859
NaI Hittorf, 1859; Dempwolff, 1904
$NaK.C_4H_4O_4$ (Küster, 1897)
$Na.NiPO_3$ (Kremann, 1903)
$NaNO_3$ Hittorf, 1859; (Chassy, 1890); (Whetham, 1895); Bein, 1898; Franklin and Cady, 1904
NaOH Wiedemann, 1856; Kuschel, 1881; (Lodge, 1886); Bein, 1898
Na_2PtCl_6 Hittorf, 1859
$Na_4P_2O_7$ Hittorf, 1859
$NaPO_3$ Hittorf, 1859; Wiesler, 1901
Na_3PO_4 Hittorf, 1859
Na_2SO_4 Hittorf, 1859; (Lodge, 1886); (Chassy, 1890); (Whetham, 1895); Masson, 1898; Goldlust, 1906
Na_2SO_3 (Daniell and Miller, 1844)
$Na_2S_2O_6$ (Daniell and Miller, 1844)
Na, UO_2 salts, see UO_2
$NaWO_4$ (Daniell and Miller, 1844)
$N(C_2H_5)_4.I$ Carrara, 1903
NH_4Cl (Daniell and Miller, 1844); Hittorf, 1856; (Whetham, 1892); Cattaneo, 1896; Bein, 1898; Masson, 1898; Hertz, 1906; Schultz, 1906
$(NH_4)_2C_2O_4$ (Daniell and Miller, 1844)

NH_4NO_3 Franklin and Cady, 1904
$(NH_4)_2O.2C_2O_3.2MO_3.3H_2O$ Rosenheim, 1896
NH_4OH Bein, 1898
$(NH_4)_2O.2MO_3$ Rosenheim, 1896
$(NH_4)_2O.2MO_3.C_2O_3$ Rosenheim, 1896
$(NH_4)_2SO_4$ (Lodge, 1886)
$(NH_4)_2SO_4.NiSO_4$ Pfanhauser, 1901
$3(NH_4)_2O.V_2O_5.4C_2O_3.4H_2O$ Rosenheim, 1896
$Ni(NO_3)_2$ (Chassy, 1890); Lussana, 1894
$NiPO_3$...Na
$NiSO_4$ (Chassy, 1890); (Lussana, 1894); Pfanhauser, 1901
$NiSO_4.(NH_4)_2SO_4$ Pfanhauser, 1901
NO_3...Ba-$KCoNH_3$
NO_3 ... Ag - Ag_3I - Ba - Ca - Cd - Co - Co.NH_3-Cu - H - Hg - K - Li - Mg - Na-$NaUO_2$-NH_4-Ni-Pb-UO_2-Zn
$NOCl_5$...RuK_2
OH ... Ba-Ca-$C_6H_5NO_2$-K-K.Co - Li-Na-NH_4-Sr
$Pb(NO_3)_2$ (Chassy, 1890); (Whetham, 1892); Lussana, 1893
PO_4...H-KH_2-Na-NaH_2-Na_2H
PO_3...H_2-Na-Na_3
P_2O_7...Na_4
$PtCl_6$...H_2-Na_2
$PtCl_4O.H_2$ Dittenberger and Dietz, 1899; Hittorf and Salkowski, 1899
Pyrone (di-methyl) (Coehn, 1902)
RbCl Bein, 1898
RuK_2NOCl_5 (Lind, 1903)
$S(CH_3)_3.I$ Carrara, 1903
$SrCl_2$ Weiske, 1857; (Lodge, 1886); Bein, 1898; Steele, 1902; Denison, 1903
Seignette salt (Küster, 1897)
$SiFl_6$...Ag
$SnCl_4$ Hittorf, 1859; Dittenberger and Dietz, 1899
SO_3 ... $Ag(C_6H_5)$ - $Ag(C_{10}H_7)$ - $Ag(C_9H_{11})$-Na_2
SO_4...Ag-$Ag(C_2H_5)$-Al-Al.K-Ca-Cd-Co . NH_3 - Cr-Cu-Fe-H-K-KC_2H_5 - K . Cu-K.Mg-Li-Mg-NH_4-NH_4Ni - Na-Ni-Tl-UO_2-Zn
S_2O_6...Ag-Na
$Sr(OH)_2$ Daniell, 1840
Strychnine hydrochloride Hittorf, 1859
TlCl Bein, 1898
Tl_2SO_4 Bein, 1898
UO_2 (acetate, chloride, citrate, glycolate, lactate, nitrate, oxalate, propionate, salicylate, sulphate, tartrate) with and without the sodium salts (Kremann, 1903)
UO_2Cl_2 Hittorf, 1859
$UO_2.CO_3$ (Luther und Krsnjavi, 1905)
$V_2O_5.3(NH_4)_2O.4C_2O_3.4H_2O$ Rosenheim, 1896
WO_4-Na
$WO_3.C_2O_3.K_2O.H_2O$ Rosenheim, 1896
Zn acetate (Chassy, 1890)
$ZnBr_2$ Kümmell, 1898
$ZnCl_2$ Moser, 1855; Hittorf, 1859; (Chassy, 1890); Kümmell, 1898; Hittorf, 1902
$Zn(CN)_2 + KCN$ Reiger, 1901
ZnI_2 Kümmell, 1898; Hittorf, 1859
$Zn(NO_3)_2$ (Chassy, 1890); Weber, 1889
ZnO_2...K
$ZnSO_4$ (Daniell and Miller, 1844); Hittorf, 1859; Moser, 1885; (Chassy, 1890); Lussana, 1893; Kümmell, 1898; Gans, 1901; Straneo, 1903

INDEX OF AUTHORS.

In the following alphabetical list, the dates furnish reference to the chronological abstract.

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Amyl Alcohol.
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THE ESTIMATION OF BORIC ACID AND BORATES IN FOODSTUFFS AND COMMERCIAL PRODUCTS.

BY R. J. MANNING AND W. R. LANG.

In a previous paper (Manning and Lang; this J., 1906, 397), a new method of estimating boric acid was described, which was found to give results in some cases to within 0·05% of the theoretical. Since the completion of this work the method has been used in the University Laboratory of Applied Chemistry and pronounced satisfactory. Its application to the determination of borates in such articles as milk, common salt, etc., is the object of this present paper, these substances being found to contain small quantities of boric acid in some form or other.

The results of this investigation are now given arranged as follows:—

(1) Two methods for the determination of borates in milk.

(2) Two methods for their determination in common methylated spirits.

(3) Two methods for their determination in commercial common salt.

Estimation of Boric Acid in Milk.

Method I.—Distillation and precipitation as barium borate.—This method is almost exactly similar to that previously published (*loc. cit.*), only, of course, adapted to the needs of the case. The first precaution necessary was to obtain milk absolutely free from boric acid and borates. About 300 c.c. of pure milk was introduced into a distilling flask and some boric acid dissolved in it, or else it was introduced in the alcohol, of which 400 c.c. were at first taken. Additions of more alcohol were made from time to time to ensure the complete distillation of the tri-ethyl or tri-methyl borate. It was now found that no matter how much boric acid was introduced in the milk that no precipitate whatever of barium borate was formed. In order to have the tri-methyl borate formed the introduction of sulphuric acid was necessary. A long series of experiments were therefore undertaken to determine what amount of sulphuric acid was necessary

with 300 c.c. of milk, as a result of which it was found that at least 70 c.c. of concentrated sulphuric acid are necessary; the large amount of water in the milk decomposes the tri-methyl compound into boric acid and alcohol. In this case the boric acid will distil over only at a very high temperature. The sulphuric acid appears to prevent this decomposition. After distilling for half an hour, the distillate was treated with a few drops of a concentrated solution of barium chloride. At this stage a slight precipitate sometimes occurred. The fats in the milk contain three esters, those of palmitic, stearic, and oleic acids. These all form compounds with barium chloride which are insoluble in water and in cold dilute hydrochloric acid. It was found that if the temperature in the distilling flask rose about 80° C., a small portion of these (probably oleic acid) was carried over. Therefore, on the addition of barium chloride, a flocculent precipitate of barium oleate appeared. This had to be removed by filtration before the experiment could be proceeded with. The distillate was now titrated against a freshly prepared concentrated sodium hydroxide solution, prepared, as before described, by dissolving newly cut pieces of sodium in water in a silver dish; phenolphthalein was used as indicator. Care had to be taken to guard against overstepping the neutral point, as the excess of the alkali united with the barium chloride to form the hydroxide. The precipitate of barium borate was now filtered off on a tared filter paper, washed carefully with alcohol, dried at 110° C., and weighed.

First of all a test series was made in order to see how small a quantity of boric acid would, on neutralisation of the distillate, give a precipitate distinctly seen by the naked eye. To this end, 50, 40, 30, 20, 10 parts boric acid were introduced into 10,000 parts of milk. The precipitate of 50 parts boric acid in 10,000 parts milk was quite heavy, the 40 less so. In this manner a gradation was obtained until when 10 parts in 10,000 was reached only a faint milkiness was obtained. This last was repeated several times with precisely the same result. Below this point traces of precipitate became untrustworthy, especially as a trace of boron compounds could be obtained from impure methylated spirits. This, however, will be dealt with later.

The results obtained from weighed precipitates were :—

Boric acid introduced.	Barium borate.	Yield.
grms.	grms.	Per cent.
1·50	2·6890	99·5
1·50	2·6830	99·3
0·50	0·8941	99·25
0·15	0·2649	98·0
0·12	0·1970	91·1
0·09	0·1414	87·2
0·06	0·0879	81·3
0·03	0·0340	63·33

Method II.—Distillation and titration.—Instead of precipitating the boric acid from the distillate as in Method I., the distillate was diluted with water up to one litre. Portions of 100 c.c. were neutralized with $N/10$ potassium hydroxide in presence of phenolphthalein. About 30 c.c. of glycerin were then added, and the titration continued until a permanent shade of pink was obtained.

Boric acid introduced.	Yield.
grms.	Per cent.
1·50	99·6
1·50	99·5
0·50	99·47
0·15	98·43
0·12	92·1
0·09	88·7
0·06	83·0
0·03	69·2

Method III.—The milk was first evaporated and afterwards charred. The charred mass was then treated with water and titrated in the presence of glycerin against potash, using phenolphthalein as indicator. The method is not yet complete and the results are temporarily withheld.

Estimation of Borates in Methylated Spirits.

Method I.—By distillation and precipitation.—The method was exactly similar to that used in the case of milk; 300 c.c. of methylated spirits and 25 c.c. of concentrated sulphuric acid were distilled until the temperature rose to 75°, when the boron compound was precipitated by barium chloride and weighed as before. One litre of methylated spirits was found to contain 0·0183 grm. boric acid as a borate of some sort.

Method II.—By distillation and titration.—Owing to the exceedingly small amounts of boric acid in the alcohol it was very difficult to obtain results that agreed. The large distillate was diluted to a known volume (500 c.c. usually), and portions of 100 c.c. taken out at a time and titrated against $N/10$ potassium hydroxide with 30 c.c. glycerin and a few drops of phenolphthalein. One litre of methylated spirits was found to contain 0·0160 grm. boric acid.

Estimation of Borates in Salt.

Method I.—By Distillation and Precipitation.—A weighed amount of common packing salt (preferably about 5 grms.) were dissolved in the necessary amount of concentrated sulphuric acid. This salt solution was now introduced with 300 c.c. of methylated spirit into a distilling flask. From this point on, the experiments were exactly similar to the previous ones. From the estimations it was found

that 100 grms. salt contain 0·88 grm. of boric acid as a bor te

Method II.—By Distillation and Titration.—Instead of precipitating the boric acid as barium borate, it was titrated against $N/10$ potassium hydroxide in the usual manner. 100 grms. of packing salt were found to contain 0·874 grm. of boric acid as a borate.

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A NEW TYPE OF CATALYSIS. THE ACCELERATION BY CHROMIC ACID OF THE REACTION BETWEEN BROMIC AND HYDRIODIC ACIDS

BY ROBERT H. CLARK

The catalytic action of chromic acid on the rate of oxidation of hydrogen iodide by bromic acid was discovered by Ostwald in the course of his "Studien zur chemischen Dynamik;"[1] and when my own work had cleared up the kinetics of the reaction in question,[2] I entered on a detailed investigation of this case of catalysis, which has yielded some very remarkable results.

The method of carrying out the measurements, the stock solutions, and the units employed in recording the results, are all as described in my previous paper, with the addition of a solution of potassium bichromate, 0.1667-F, and another 0.001251-F, which were standardized against the acid by means of a solution of caustic potash and phenolphthalein. In the tables the number of cubic centimeters of 0.00125-F bichromate[3] is given under *Cr*.

As in the reaction between bromic and hydriodic acids, the presence of air had no material effect on the results of the measurements; and small quantities of iodine, such as are liberated during the reaction, exerted little or no effect on the rates.

Effect of the Bichromate on the Rate

The fact that the increased liberation of iodine in presence of chromic acid is not accompanied by a proportional reduction of the latter was observed by Ostwald, who found also that the increase in rate is proportional to the concentration of the chromic acid. Both these conclusions are supported by the measurements of Table I. In the first place, the

[1] Zeit. phys. Chem., **2**, 138 (1888).

[2] Jour. Phys. Chem., **10**, 679 (1906).

[3] 0.00125 gram-formula-weights $K_2Cr_2O_7$ per liter.

TABLE I

$KBrO_3$, 20.5; KI, 98.67; HCl. 95.15; Vol., 250 cc; Temp., 30° C.

t	Cr	x	x'	R_0	Ac/Cr	t	Cr	x	x'	R_0	Ac/Cr
5	0	0.19	0.19	0.038	—	10	0	0.38	0.385	0.038	—
5	2	0.35	0.354	0.071	0.017	10	2	0.70	0.71	0.071	0.016
5	4	0.50	0.505	0.10	0.015	10	4	0.95	0.97	0.097	0.015
5	6	0.65	0.659	0.13	0.015	10	6	1.25	1.28	0.13	0.015
5	10	0.97	0.98	0.20	0.016	10	10	1.92	1.99	0.20	0.016
5	12	1.17	1.20	0.24	0.017	10	12	2.30	2.40	0.24	0.017
5	14	1.29	1.33	0.27	0.016	10	14	2.55	2.67	0.27	0.018
5	16	1.48	1.52	0.30	0.016	10	16	2.90	3.14	0.31	0.017
5	18	1.64	1.70	0.34	0.017	10	18	3.22	3.39	0.34	0.016
5	20	1.83	1.89	0.38	0.017	10	20	3.55	3.77	0.38	0.017

values of x' for $t = 10$ are just double those for $t = 5$, therefore no perceptible diminution in the concentration of the bichromate (reduction) can have occurred in the interval. In the second, the rate of liberation of iodine (R_0) is not proportional to the concentration of bichromate, but the acceleration:

$$Ac = R_0 - R_0(Cr = 0)$$

is; this is shown by the constancy of the quotient Ac/Cp, and graphically in Fig 1. The experiments of Table II, more-

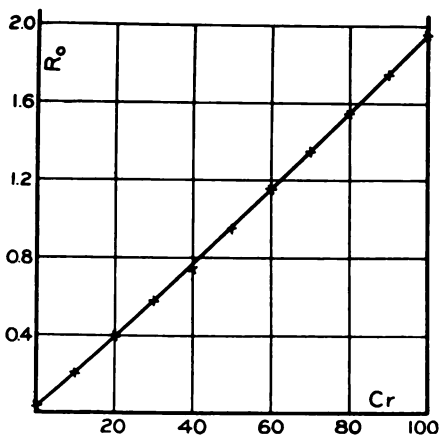

Fig. 1

TABLE II

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15; Cr, 2.0; Vol., 250 cc; Temp., 30° C.

t	x	x'	R_0
240	13.95, 14.07, average 14.01	19.83	0.083
300	16.33, 16.33, " 16.33	24.65	0.082

$$\frac{24.65 - 19.83}{300 - 240} = 0.080$$

over, show that even after the reaction had proceeded for four hours during which the additional iodine liberated because of the presence of the bichromate was oxidimetrically equivalent to 56 percent of the latter, there was no diminution in the rate of liberation of iodine except that due to the fall in the concentrations of the bromate, iodide and acid, which was allowed for in computing R_0.

EFFECT OF THE CONCENTRATIONS OF BROMATE, IODIDE AND ACID ON THE RATE

Systematic measurements were undertaken to ascertain the effect of changes in the concentration of each of the reagents in turn, on the rate of liberation of iodine. The results, which are contained in Tables III-VI, show that the rate is

TABLE III

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30° C.; $t = 5$

Cr	x	x'	R_0	Cr	x	x'	R_0
0	0.19	0.19	0.038	18	1.64	1.70	0.34
1	0.25	0.253	0.05	20	1.83	1.89	0.38
2	0.35	0.354	0.07	30	2.70	2.83	0.57
3	0.40	0.404	0.08	40	3.50	3.71	0.74
4	0.50	0.505	0.10	50	4.35	4.69	0.94
6	0.65	0.659	0.13	60	5.25	5.74	1.15
8	0.81	0.82	0.16	70	6.07	6.73	1.35
10	0.97	0.98	0.20	80	6.95	7.82	1.56
12	1.17	1.20	0.24	90	7.65	8.71	1.74
14	1.29	1.33	0.27	100	8.35	9.73	1.95
16	1.48	1.52	0.30				

TABLE IV

$KBrO_3$, 20.5 × f; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30°C

t	Cr	f	x	x'	R_o
5	10	2	2.00	2.07	0.41
5	12	2	2.33	2.42	0.48
5	14	2	2.60	2.71	0.54
5	16	2	2.95	3.10	0.62
5	18	2	3.27	3.45	0.69
5	20	2	3.57	3.78	0.76
5	6	3	2.01	2.02	0.40
5	10	3	2.87	3.01	0.60
5	14	3	3.82	4.06	0.81
10	18	2	6.30	7.01	0.70
10	20	2	6.80	7.61	0.76

TABLE V

$KBrO_3$, 20.5; KI, 98.67 × f; HCl, 95.15; Vol., 250 cc; Temp., 30° C

t	Cr	f	x	x'	R_o
5	10	2	2.00	2.07	0.41
5	12	2	2.32	2.41	0.48
5	14	2	2.58	2.68	0.54
5	16	2	2.94	3.06	0.61
5	18	2	3.24	3.40	0.68
5	20	2	3.58	3.77	0.76
5	6	3	2.00	2.01	0.40
5	10	3	2.87	2.99	0.60
5	14	3	3.80	4.00	0.80
10	16	2	5.70	6.23	0.62
10	18	2	6.30	6.93	0.69
10	20	2	6.79	7.52	0.75

TABLE VI

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15 × 2; Vol., 250 cc; Temp., 30° C; $t = 5$

Cr	x	x'	n, 1st appx.	n, 2nd appx.	R_o
0	0.90	0.91	2.00	2.00	0.18
2	1.17	1.19	1.72	1.73	0.24
4	1.48	1.51	1.58	1.58	0.30
6	1.86	1.91	1.52	1.53	0.38
8	2.22	2.30	1.45	1.49	0.46
10	2.58	2.68	1.41	1.44	0.54
12	2.97	3.10	1.35	1.37	0.62
14	3.27	3.42	1.34	1.36	0.68
16	3.61	3.83	1.29	1.32	0.77
18	3.96	4.21	1.27	1.30	0.84
20	4.30	4.60	1.23	1.28	0.92
30	6.05	6.63	1.16	1.22	1.33
40	7.44	8.32	1.09	1.13	1.66
50	9.00	10.30	1.03	1.12	2.06
60	10.30	12.04	0.97	1.07	2.41
70	11.50	14.17	0.93	1.05	2.83
80	12.95	15.71	0.90	1.01	3.14
90	14.19	17.63	0.89	1.01	3.53
100	15.22	19.24	0.87	0.96	3.85

proportional to the concentration of the bromate and to that of the iodide (the same as in absence of chromate); but that the effect produced by changing the concentration of the acid depends on the amount of bichromate present.

The experiments of Table III serve as standard for comparison, while in the other three the concentrations of bromate, iodide and acid respectively were multiplied by the variable factor f. Under R_o in the last column is entered the "initial rate"

$$R_o = dx/dt(x = o) = x'/t$$

that is, the number of cubic centimeters of hundredth-normal iodine liberated per minute in a solution of the composition indicated at the head of the table.

Method of computing x' and n

The general differential equation connecting the rate of

liberation of iodine with the concentrations of the reagents may therefore be written:

$$dx\,dt = K(A-x)(B-x)(C-x)^n(1 - M.Cr) \qquad (1)$$

where A, B and C are the concentrations of the bromate, iodide and acid respectively, and n depends on the concentration of the bichromate; K and M are constants.

By comparing the iodine readings (x) from Tables III and VI, in the latter of which the concentration of the acid was double that in the former, a first approximation to the values of n was obtained:

$$n\ first\ approx. = \frac{log\ x\ (Table\ VI) - log\ x\ (Table\ III)}{log\ 2} \qquad (2)$$

The values so computed are entered in Table VI under "*n first approx.*" These approximate values were then introduced into Equation (1), which was integrated by series, and used to obtain a first approximation to the values of x' for Table VI.

$$x' = KABC^n t(1 + M\,Cr) = x + (1{\cdot}2A - 1{\cdot}2B - n{\cdot}2C)x^2 +$$
$$1{\cdot}3A^2 - 1{\cdot}3B^2 - \overline{n^2 - n}\,6C^2 + 1{\cdot}3AB - n{\cdot}3AC - n{\cdot}3BC)x^3 \qquad (3)$$

A second approximation to the true value of n was then made, using x' (Equation 3) in place of x in Equation (2); the numbers so obtained are entered under "*n second approx.*" in Table VI. Fig. 2 shows these values of n plotted as a

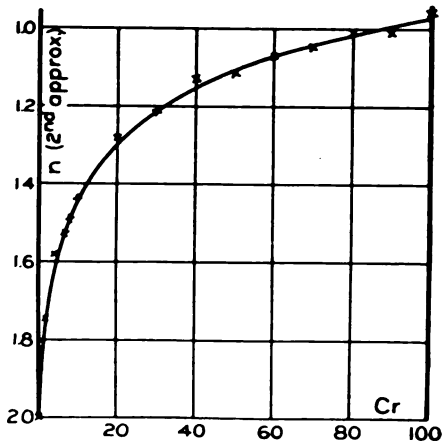

Fig. 2

function of Cr. When $Cr = 0$, the rate is proportional to the second power of the concentration of the acid; on addition of potassium bichromate the power diminishes until $Cr = 80$, when the rate is proportional to the first power of the concentration of the acid, and the curve (Fig. 2) becomes a straight line.

In Ostwald's "Lehrbuch der Allgemeinen Chemie" II (2), p 262, that author says: "So long as the catalyser is neither altered, formed, nor destroyed by the reagents or products of the reaction, its influence is exerted only on the value of the velocity constant, and not on the character of the kinetic equation." The present case is evidently an exception.

Interpretation of the Results

These results may be expressed by assuming that:

(*i*) In solutions containing bromate, bichromate acid and iodide, two reactions take place simultaneously, both resulting in the liberation of iodine.

(*ii*) The rate of the first reaction is proportional to the concentrations of the bromate, and iodide and to the square of that of the acid; while that of the second is proportional to the concentrations of bromate, iodide and acid, and slightly less than proportional to that of the bichromate.

(*iii*) The second reaction takes place without proportional reduction of the bichromate.

The corresponding kinetic differential equations are:

$$\partial x/dt = K_1(A - x)(B - x)(C - x)^2, \text{ and}$$
$$\partial x/dt = K_2(A - x)(B - x)(C - x)Cr$$

and the rate at which iodine is liberated in the solution:

$$dx/dt = (A - x)(B - x)(C - c)(K_1\overline{C - x} + K_2Cr) \qquad (4)$$

The values of the two constants in this equation were calculated from the two experiments of Table VI in which $Cr = 0$ and $Cr = 100$ respectively; they are, $K_1 = 645 \times 10^{-12}$ and $K_2 = 333 \times 10^{-10}$. The change of n with the concentration of the bichromate (Table VI and Fig. 2) is in quantitative accord with these assumptions, as may be seen by

comparing the values of "*n second approx*" in Table VI with those calculated from the equation:[1]

$$n\ calc. = \frac{log(2K_1C + K_2Cr) - log(K_1C + K_2Cr)}{log\ 2} + 1 \qquad (5)$$

Temperature Coefficient

In order to find the temperature coefficients of the rates involved, I repeated the experiments of Table IV at zero. (See Table VII.)

Table VII

Cr	*n*, 2d appx.	*n* calc.	Cr	*n*, 2d appx.	*n* calc.
0	2.00	2.00	20	1.28	1.26
2	1.73	1.75	30	1.22	1.19
4	1.58	1.62	40	1.13	1.12
6	1.53	1.53	50	1.12	1.11
8	1.49	1.47	60	1.07	1.10
10	1.44	1.41	70	1.05	1.09
12	1.37	1.37	80	1.01	1.07
14	1.36	1.34	90	1.01	1.06
16	1.32	1.30	100	0.96	1.04
18	1.30	1.28			

Under "coeff" is entered the temperature coefficient, that is the cube root of the ratio of the two rates R_0 at 30° and at 0°. The coefficient varies with the amount of bichromate present, as is shown graphically in Fig. 3; the similarity between this curve and that of Fig. 2 furnishes another argument in support of the assumption of two simultaneous reactions. The coefficient falls off gradually as the quantity of bichromate increases until $Cr = 60$, when it becomes constant at 1.19; this may be taken as the temperature coeffi-

[1] In Table VI the concentration of the acid was twice that in Table III; hence, comparing values of R_0 from experiments in which the concentration of bichromate was the same,

by Equation (1) $\frac{R_0\ (Table\ VI)}{R_0\ (Table\ III)} = 2^n$

by Equation (4) $\frac{R_0\ (Table\ VI)}{R_0\ (Table\ III)} = \frac{2(2K_1'C + K_2'Cr)}{K_1'C + K_2'Cr}$

Equation 5 is obtained by equating these two expressions and taking the logarithms; C refers to the acid of Table III.

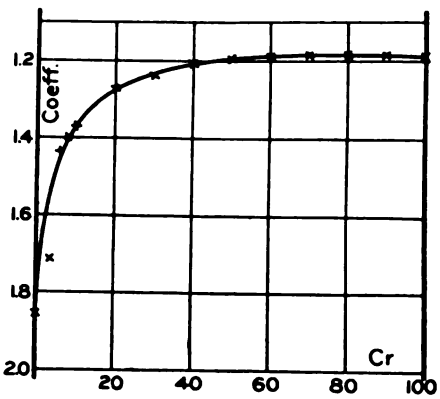

Fig. 3

cient of the second reaction of page 359, while that of the first is 1.85.

TABLE VIII

$KBrO_3$, 20.5; KI, 98.67; HCl, 190.3; Vol., 250 cc; Temp., 0° C; $l = 5$

Cr	x	x'	R_o	Coeff.
0	—	—	—	1.85[1]
4	0.30	0.30	0.06	1.71
6	0.63	0.63	0.13	1.43
8	0.85	0.87	0.17	1.40
10	1.05	1.07	0.21	1.37
12	1.25	1.27	0.25	1.35
14	1.42	1.45	0.29	1.33
16	1.76	1.80	0.36	1.29
18	1.91	1.95	0.39	1.29
20	2.10	2.16	0.43	1.28
30	3.29	3.45	0.69	1.24
40	4.45	4.75	0.95	1.21
50	5.45	5.91	1.18	1.20
60	6.45	7.09	1.42	1.19
70	7.25	8.08	1.62	1.19
80	8.15	9.18	1.84	1.19
90	9.00	10.28	2.06	1.19
100	9.72	11.24	2.25	1.19

[1] This Journal, 10, 679 (1906).

CHROMIC ACID AND THE ANALOGOUS REACTIONS

The difficulty of inventing any hypothetical mechanism to explain the part played by the bichromate is enhanced by the circumstance that this case stands alone. Mr. Dushman[1] has shown that potassium bichromate is without action on the rate of the reaction between iodic and hydriodic acids; and by means of a few measurements I have ascertained that the rates of the reactions between

Iodic and hydrobromic acids
Bromic and hydrobromic acids
Chloric and hydrobromic acids and
Chloric and hydriodic acids

are likewise uninfluenced by the presence of potassium bichromate.

Summary

(1) Addition of potassium bichromate to a solution containing bromic and hydriodic acids brings a new reaction into operation, which consists in the liberation of iodine at a rate proportional to the concentrations of the bromate, iodide, bichromate and acid, without reduction of the bichromate. The normal reaction, whose rate is proportional to the concentration of the bromate and iodide and to the square of that of the acid, goes on unaffected by the presence of the bichromate.

(2) The processes of oxidation of hydriodic and hydrobromic acids by the oxyacids of the halogens, other than that of hydriodic by bromic acid, are not affected by the presence of potassium bichromate. Although in other respects the members of this group of reactions resemble one another closely from the kinetic point of view as well as from that of pure chemistry, the analogy fails at this point.

In both respects this case of catalysis is unique.

I desire to express my thanks to Prof. W. Lash Miller, under whose direction these measurements were carried out in the winter of 1904-5.

[1] Jour. Phys. Chem., 8, 453 (1904).

The University of Toronto
February, 1907

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